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THE INSTITUTE OF PETROLEUM

SYMPOSIUM ON INSULATING OILS

FIRST SESSION

AN Ordinary General Meeting of the Institute of Petroleum was held at the Institution of Electrical Engineers, Savoy Place, London, W.C.2, on 5 March 1958, in two sessions, the Chair being taken by Professor F. Morton, Member of Council.

The minutes of the previous meeting were confirmed and signed as a correct record. The names of members elected since the previous meeting were also announced.

Professor Morton then invited P. W. L. Gossling to take the chair for the presentation and discussion of the papers in the Symposium on Insulating Oils.

P. W. L. Gossling: In opening this Symposium on Insulating Oils we welcome the presence of a large number of members of the Institution of Electrical Engineers, whose own premises we are very grateful to be able to use to-day. We are very honoured to have with us so many visitors from overseas. Particularly would I mention Professor Henri Weiss, whose work for many years as Chairman of the Oil Committees of the International Electrotechnical Commission and of CIGRE is well known to many of you. We have also from France Dr T. Salomon, who has for many years collaborated with Professor Weiss. I have to say with regret that Dr van Rysselberge, the secretary of the IEC Committee, who was to have been with us, has a serious illness. Dr van Rysselberge has recently given several papers on certain aspects of the work which we are to discuss. I would also specially mention H. Liander from Sweden, whose work with soluble catalysts, first described at a CIGRE meeting in 1948, showed their special suitability for oxidation tests on transformer oils. In the following year investigations with these catalysts were taken up by IEC, and they have since remained an important feature of their programmes. We have to welcome, too, Dr L. Maurer, chief engineer of the Transformer Works of Siemens Schuckert, Nuremburg, and Chairman of the German Oil Committee. We have with us also G. Ericson, chief chemist of the ASEA Company of Sweden and a colleague of Mr Liander.

All the gentlemen whom I have mentioned have taken an active part in IEC work on transformer oil. There are also a number of other visitors from abroad whom we welcome. These greetings are offered on behalf of the Institute of Petroleum, the Electrical Research Association, and the Institution of Electrical Engineers.

This symposium is the second which has been devoted by the IP solely to insulating oils, and one object of this introduction is to link the two so as to secure a useful degree of continuity.

Reverting to the 1946 meeting, it may be recalled that, in the discussion itself, operating difficulties in service dominated, although from data given it appeared that, even then, serious trouble was not proportionately frequent. There was, however, an overwhelming opinion that more difficulty, especially with regard to acidity and its effects, had resulted from the use of the more highly refined class "A" oil than from class "B." The 1951 version of the transformer oil specification BS 148 dealt with this position by adding a test for acidity development in the Sludge Test, and fixed a maximum for acidity, making it virtually impossible to meet the specification with over-refined oils, as those of class "A" had widely been called.

The discussion in 1946 also made it clear that several transformer manufacturers accepted the fact that oil deterioration was influenced by other insulating materials, with special emphasis upon varnishes. The experience was several times cited of pairs of identical transformers sharing the load in the same substation, one suffering oil trouble while the other behaved satisfactorily. Reference was made also to the occasional incidence of green coloration in the oil and, reconsidering all the evidence, it seems that the cause of such troubles was most likely the occasional failure of manufacturers to ensure the complete transformation of the varnish into oil-insoluble film.

Among the present papers, that by Professor F. Morton and R. T. T. Bell, in addition to providing a valuable general survey of the literature upon liquid phase oxidation, bridges the gap from the last symposium in the foregoing regard. The summary of the more recent work dealing with auto-retardation in the oxidation process, in particular that due to the presence of certain types of aromatic hydrocarbons, makes clear the importance of the latter as constituents of transformer oils to the revised specifications (see, for example, Appendix B of the paper by C. N. Thompson at this meeting). With regard to the varnish problem, Morton and Bell draw attention to Massey's comprehensive work, published by the IP in 1952. It is seen later that the catalytic effect of soluble copper compounds, which can readily be formed on copper surfaces when certain types of varnish are incorrectly cured, is a subject of much current interest.

The postulate of George and Robertson, stated at the 1946 meeting, that the initiation of uncatalysed oxidation involves energy chains, has not been accepted universally; Morton and Bell summarize the alternatives, including the possibility of initiation by the oxygen molecule directly, without the intervention of free radicals.

In the catalysed reaction the process of initiation by free radical formation appears to be more generally acceptable and, catalysed or uncatalysed, the hydroperoxide is formed, the reaction then being propagated by the breakdown of hydroperoxide, leading to more free radicals, so providing for a chain reaction until termination products are formed. At the present meeting J. C. Robb and L. M. Shahin describe a novel method of investigating the rate of propagation, by measurement of the heat evolved. The selection of *cyclo*hexene for study had no special significance in the context of this symposium, but was convenient for the first work. Professor Robb, who is Professor of Physical Chemistry at the University of Birmingham, is engaged on further work for ERA using this novel method for measuring oxidation rates. It is proposed to work upon hydrocarbons selected

from those likely to be present in transformer oil, or at least typical of such. It is hoped that the method will be applicable to the direct measurement of the retardation of oxidation by admixture, for example, of aromatic hydrocarbons with naphthenes, so making it possible to determine the chemical types affording maximum oxidation stability.

It may be mentioned that Professor Morton's original report, No. E/T65, prepared for ERA in 1954 and 1955, concluded with recommendations that work in the following four directions would be of specific interest:

(1) changes in reaction mechanism with increase in temperature, particularly in the metal-catalysed reaction;

(2) the role of solid copper catalyst and the mechanism by which the copper ion passes from the metallic surface to the insoluble precipitate;

(3) further studies of the relationship between oxidation characteristics and chemical constitution, particularly the behaviour of polynuclear aromatic hydrocarbons, and heterocyclic sulphur and nitrogen compounds;

(4) mechanism of inhibitor action and the relationship between composition of an oil and its inhibitor response.

It is clear that the work of Robb and Shahin finds a useful place to items (3) and (4) in the above scheme.

In the next paper of this series, by C. E. H. Bawn and D. P. Moran, the mechanism of the catalytic processes involved in hydrocarbon oxidation is studied. Professor Bawn is the Grant-Brunner Professor of Inorganic and Physical Chemistry at Liverpool University, where further work for ERA is in progress. The introductory summary in the paper of the existing evidence for the formation of complexes of the metal in catalysed oxidation is very informative. In the experimental work the correlation found between oxygen absorption and hydroperoxide formation, showing the part played by hydroperoxide in propagating the reaction, is very convincing. The evidence for the formation of metal complexes with hydroperoxide may be linked up with the work reported by Thompson in another paper to this symposium. The results of the study of the addition of successive amounts of catalyst (Bawn and Moran) are exactly analogous to those found by Liander in his investigation of transformer oil oxidation with soluble copper catalyst. Bawn and Moran suggest that the initiation of the catalysed reaction may be dependent upon the existence of small amounts of hydroperoxide, possibly formed by the mechanism of uncatalysed oxidation. The whole of this experimental work is clearly a valuable contribution to Professor Morton's suggested investigation by ERA.

In C. N. Thompson's paper we are brought to the vexed question of the mechanism of metallic-copper-catalysed oxidation—is it heterogeneous or homogeneous, *i.e.* a purely surface effect or dependent on the solution of copper as the first stage?

It is perhaps useful at this point to consider the background as given in the second paper of this series, namely, the ERA/IEC work in the last decade. It is reported that, starting at the meetings of CIGRE in 1948 and IEC Technical Committee No. 10 in 1949, the delegates of Belgium, France, Great Britain, Holland, Italy, Switzerland, and the U.S.A. have pursued a series of programmes aiming at the development of an internationally acceptable oxidation test. Agreement was reached upon a tentative method in 1954, with the reservation by some that the method was of unduly long duration.

The method used a simple test tube for the oil, through which oxygen was blown while the temperature was maintained at 100° C. Using metallic copper wire as catalyst, it was found that a duration of 164 hours was required for the formation of reasonable amounts of oxidation products. If the copper wire was replaced by copper or iron naphthenate in solution in the oil, with a metal concentration of 10 p.p.m., the rate of oxidation was much greater and the possibility of test durations of only 48 hours was visualized. Several countries considered a test of this short duration much to be desired, so the possible use of soluble catalyst was of great interest. In addition, it was claimed by some that a greater precision was obtainable with soluble catalyst than with the metal, and the work has certainly shown that there exists considerable room for improvement in this regard with the metallic catalyst. On the other hand, the use of soluble catalyst has been strongly opposed in some quarters, as discussed in the introduction to Thompson's paper, essentially because some oils are more prone than others to attack copper surfaces. Hence a test with soluble metal added at fixed concentration might penalize oils which are less active in this regard.

Thompson now describes a series of experiments, made in the laboratories of three oil companies collaborating through ERA, allowing the conclusion to be drawn that a more important difference between oils is the degree to which copper in solution, derived from the metal surface or added in the soluble state, is changed into an insoluble form which is inactive. With the oils used in this work it was shown that "the so-called variable corrosivity effect . . . can be ignored, because it is completely overshadowed by the copper precipitation reaction." It is concluded that, in the catalysis of oil oxidation by metallic copper, the only important mechanism is of homogeneous type.

THE LOW TEMPERATURE LIQUID PHASE OXIDATION OF HYDROCARBONS: A LITERATURE SURVEY*

By FRANK MORTON† (Fellow) and R. T. T. BELL†

REFINED mineral oils, used in transformers as fluid dielectric and heat transfer media, deteriorate in time with the formation of sludges, acids, water, and other products. This deterioration is the result of oxidation of the hydrocarbons, accelerated by certain catalysts such as copper. Mineral oils with high resistance to oxidation are produced by acid treatment or solvent refining of selected crude oil fractions, but a limit is imposed on the choice of fraction by the inclusion of a pour point in the specification. Un-

* Based upon Report No. E/T 65 of the Electrical Research Association, whose permission to use this is acknowledged.

† Dept. of Chemical Engineering, College of Science and Technology, Manchester.

fortunately, specifications for transformer oils vary from country to country, and the acceptance tests—particularly the oxidation test—also vary. In an attempt to produce an internationally acceptable test for oxidation stability a great deal of experimental work has been carried out, but correlation of some of this work is difficult because of the variety of hydrocarbon oils which have been used. Even within the limits of a single specification, the hydrocarbon composition of the oil may vary over a wide range.

The high temperature oxidation of hydrocarbons has been studied by many workers to establish the mechanism of combustion and flame propagation. Excellent reviews have been given by Semenov [1] (1935) and Lewis and von Elbe [2] (1938), in which the chain character of the gas phase reaction is shown to be well established. Recent conferences on combustion also show a surprising agreement among research workers concerning the reaction steps involved in the overall combustion of hydrocarbons. Low temperature (below 200° C) liquid phase oxidation of hydrocarbons has been studied for a variety of reasons. The air blowing of heavy oils to produce asphalts was perhaps the first commercial application of liquid phase oxidation, but the attempted production of fatty acids for manufacture of synthetic fats and soaps during 1914–18 by the oxidation of mineral oils represents the first attempt to produce individual oxidation products by catalysed air oxidation. The deterioration of lubricating oils in service, the oxidation of transformer and other electrical oils, and the production of gums and bad colour in storage of motor fuels have all demanded an investigation of the oxidation of hydrocarbons. The possibility that controlled oxidation of individual hydrocarbons might lead to commercially important organic chemicals has led to many investigations which contribute perhaps the greatest body of evidence concerning the course of the reaction. Finally, the complexity of products, the phenomenon of autoxidation, and the properties of catalysts and inhibitors have aroused interest in the mechanism of the reaction, and much experimental work has been devoted to a study of its kinetics. Excellent reviews of these many-sided activities have been published by Ellis [3] (1937), Egloff, Schaad, and Lowry [4] (1929), and more recently by Zuidema [5] and Frank.[6]

The object of this paper is to review the published work on the liquid phase oxidation of hydrocarbons and the theories advanced concerning the reaction mechanism, and to relate this knowledge to the behaviour of transformer oils in practice and in acceptance tests. In view of the complete review of the literature prior to 1937 given by Ellis [3] and the more recent reviews of Zuidema,[5] Goldstein,[7] and Brookes,[8] no attempt will be made to cover the whole of what has been published, although it is hoped that all the relevant work up to 1955 has been considered.

PURE HYDROCARBONS

The major difficulty in the early studies of the oxidation of hydrocarbons lay in the isolation of the primary products. Bone and his co-workers [9] believed that the first product was an alcohol and that subsequent products were formed by oxidation of the alcohol. Later work has shown that alcohols are in general less easily oxidized than the corresponding hydrocarbon, and that in certain cases the alcohols act as oxidation inhibitors. For these reasons the "hydroxylation" theory can no longer be held tenable for the low temperature reaction.

The basis of modern theory lies in the assumption that the primary reaction product between a hydrocarbon and oxygen is a peroxide, or rather a hydroperoxide. This view was first advanced by Bach [10] (1897) and Engler and Wild [11] (1897–98) and subsequently developed in more detail by Callender [12] (1927) and Ubbelohde [13] (1935).

In 1939 Criegee [14] was able to show that *cyclo*hexene gave a hydroperoxide in which the peroxide group was attached to the carbon atom adjacent to the double bond and in which the double bond was preserved. Farmer and his co-workers [15] (1942) investigated the oxidation of a number of olefins and demonstrated that in general the unsaturation of the olefins was preserved and peroxide formation occurred on the carbon atom adjacent to the double bond.

The obvious analogy with the autoxidation of aromatic hydrocarbons which oxidize on the $-CH-$ group vicinal to the benzene ring (*cf.* Chavanne [16] and Stephens [17]) led to an extensive study of these compounds and to the extension of the "peroxide" theory to the autoxidation of hydrocarbons in general.

Stephens did not isolate peroxides except from *cyclo*hexene, but subsequent studies of the oxidation of ethylbenzene by several workers indicate that the formation of a peroxide on the $-CH_2-$ group is undoubtedly the first step in this reaction.[18]

Decalin and tetralin proved to be particularly suitable hydrocarbons for kinetic study of the autoxidation process. The oxidation proceeds at reasonable speed, even in dilute solution in chlorobenzene, and yields easily separable crystalline hydroperoxides. Tetralin in the absence of catalysts autoxidizes in four distinct stages [19]:

(1) An induction period lasting some hours in which the oxygen uptake is very small and can be followed only by analysis of the peroxide content of the hydrocarbon.

(2) An auto-catalytic stage in which the rate of absorption of oxygen accelerates until the peroxide content is about 5 per cent.

(3) A steady state with constant but fairly rapid absorption of oxygen continuing until about 40 per cent of the tetralin has been oxidized.

(4) A decrease in the rate of oxygen absorption

while there still remains a considerable percentage of unchanged hydrocarbon in the reaction mixture.

In the first two stages the hydroperoxide is formed almost quantitatively, but some decomposition of the peroxide is evident in the third stage, and this increases in the final stage. The kinetics of this process have been analysed by Medvedev [20] (1939), Ivanov [21] (1939), and further studied by Robertson and Waters [22] (1946), etc. Medvedev suggested that the process proceeds by two consecutive chain reactions both involving free radicals and that decomposition of the peroxide gives rise to new active molecules which initiate secondary chains. This view is substantiated by the fact that the hydroperoxide is a marked catalyst for the process, its addition (5 per cent) to a peroxide-free sample of tetralin reducing the induction period to zero. Since the peroxide is also a catalyst for such chain reactions as the polymerization of styrene, etc., it is believed that the peroxide acts by dissociation into free radicals which can bring about the normal oxygen-uptake cycle.

Since the peroxide is an immediate catalyst for the autoxidation of tetralin and since several other " free radicals " such as free phenyl radical from dibenzoyl peroxide are also immediate catalysts (*i.e.* reduce the induction period to zero), Waters has suggested that these catalysts—as well as certain strong oxidizing agents—act by abstracting hydrogen atoms from the autoxidizable hydrocarbon.

$$X\cdot + \overset{|}{\underset{|}{C}}H_2 \longrightarrow XH + \overset{|}{\underset{|}{C}}H\cdot \quad . \quad . \quad (1)$$

George and Robertson,[23] however, consider that the initial step in the uncatalysed autoxidation process involves energy chains rather than free radicals.

$$RH \longrightarrow R^*H \longrightarrow R^* \quad . \quad . \quad (2)$$

This question of the initiation of the reaction sequence will be discussed later, and is obviously of considerable importance to an understanding of the autoxidation of mixed hydrocarbons such as transformer oils, etc.

With this reservation—that the initiation step is not entirely free from question—the steps in the reaction sequence are generally accepted to be as follows:

Initiation—

$$RH \xrightarrow{\text{activation}} R\cdot + (H\cdot) \quad . \quad . \quad . \quad (3.1)$$

Propagation—

$$R\cdot + O_2 \longrightarrow R{\cdot}O{\cdot}O\cdot \quad . \quad . \quad . \quad . \quad (3.2)$$
$$R{\cdot}O{\cdot}O\cdot + RH \longrightarrow R{\cdot}O{\cdot}OH + R\cdot \quad (3.3)$$

Termination—

$$R\cdot + R\cdot \longrightarrow RH + R(-H) \quad . \quad . \quad (3.4)$$
$$RO_2\cdot + \cdot OH \longrightarrow ROH + O_2 \quad . \quad . \quad (3.5)$$
$$R\cdot + R\cdot \longrightarrow R{-}R. \quad . \quad . \quad . \quad . \quad (3.6)$$

etc.

The reaction is catalysed immediately by free radicals such as phenyl radicals from dibenzoyl peroxide or benzene diazonium acetate, and more slowly (*i.e.* there is still an induction period) by metals such as copper, cobalt, zinc, etc., either as free metals or as soluble metal salts. The reaction is inhibited (*i.e.* the induction period is increased) by small quantities of " inhibitors " which are invariably easily oxidizable compounds such as phenols, thiols, amines, or alcohols. Since similar compounds may be formed by the breakdown of the hydroperoxide, the eventual retardation of the autoxidation reaction of hydrocarbons is in part due to such inhibitors. There is some difference between the kinetics of the catalysed and uncatalysed oxidation of hydrocarbons (*e.g.* tetralin), for which reason George and Robertson suggest that the uncatalysed reaction is initiated by energy chains, whereas the catalysed reaction is undoubtedly a free radical mechanism. The kinetics and reaction mechanisms have been discussed at some length in various reviews and symposia. It is sufficient for the purpose of this résumé to note

(*a*) That although the initiation of the reaction by added free radicals or by photochemical means is clearly established, the mechanism of the initiation of the reaction between oxygen and the hydrocarbon in the liquid phase in the absence of any such free radical forming mechanism is not entirely understood (*cf.* George and Robertson [23] and Kenner [24]).

(*b*) A variety of reactions have been postulated as " terminating " reactions, which lead to the formation of ketones, with or without chain-breaking, or to the polymerization (at least dimerization) of the hydrocarbon.

(*c*) Subsequent oxidation of the initial breakdown products will proceed, probably also by chain reactions, leading to formation of acids, etc.

(*d*) The reaction is independent of oxygen pressure provided oxygen is present in sufficient quantities. At low oxygen pressures, or with limited availability of oxygen, the rate of diffusion of oxygen becomes the rate-controlling step.

(*e*) The position of initial oxygen attack has been established in many cases. Twigg [25] has found that the secondary carbon atoms of *n*-decane are attacked equally, and preferentially to the primary carbon atoms. Hoffmann and Boord [26] give the following order of preference for the initially oxidized carbon atoms of ethyl-*cyclo*hexane

TABLE I

Oxidation of Benzene Aromatics

Data from Stephens and Stephens and Roduta.

Hydrocarbon	Oxidation temp °C	Conditions (time) hours	Grams of products per 100 g of hydrocarbon
Toluene	100	48	Trace of aldehyde
m-Xylene	100	30	2·1 g toluic aldehyde; 1·1 g toluic acid
Mesitylene (1,3,5-trimethylbenzene)	100	24	2·1 g 1,3-dimethylbenzaldehyde; 1·4 g mesitylenic acid
Durene (1,2,4-tetramethylbenzene)	100	9	5·8 g durylic aldehyde; 4·9 g durylic acid
p-Cymene (1-methyl-4-*iso*propylbenzene)	—	—	1·2 g cumic aldehyde; 0·8 g cumic acid
	102–104	14	Cumic aldehyde; cumic acid; 2 g *p*-tolyl methyl ketone; formic acid
Ethylbenzene	110–115	24	19 g acetophenone
n-Propylbenzene	102–104	25	Resin
	78	36	Trace of propiophenone
Cumene (*iso*propylbenzene)	102–104	23	4 g acetophenone
	80	32	Formic acid
tert-Butylbenzene	102–104	25	Trace of non-volatile residue
Ethylmethylphenylmethane	119	14–29	2–10 g acetophenone
	140	90	7·5 g acetophenone; 4·2 g benzoic acid
n-Butylmethylphenylmethane	119	14–29	2–10 g acetophenone; butyric acid identified by odour
Methyldiphenylmethane	119	14–29	2–10 g benzophenone, formic acid
Triphenylmethane	119	14–29	2–10 g benzophenone, phenol
Diphenylmethane	119	14–29	2–10 g benzophenone

TABLE II

Oxidation Products of Five Classes of Hydrocarbons

Data taken from Larsen, Thorpe, and Armfield; all values expressed as percentage of total oxygen consumed.

Class of hydrocarbon	% O_2 consumed							
	Free acid	Combined acid (ester)	Peroxide	Alcohol and phenol	Carbonyl	H_2O	CO_2	Volatile acids
Paraffin	14·3	16·3	4·1	1·9	46·0	43·9	4·7	—
Naphthene and alkylnaphthene	11·2	17·0	13·5	8·9	51·4	21·9	3·8	0·6
Aromatic naphthene	6·1	23·1	4·3	8·5	27·2	16·7	1·2	0·4
Alkylbenzene	9·5	12·7	6·7	3·3	36·3	18·2	6·5	Trace
Naphthalene and alkylnaphthene	6·9	16·3	1·4	9·4	9·6	51·3	7·8	1·6

TABLE III

Oxidation of Lubricating Oils

Data from Larsen *et al.*; all values expressed as percentage of total oxygen consumed.

Oil	Temp. of oxidation, °C	O_2 absorbed, cc per 100 g	% O_2 consumed								Asphaltene (mg per 10 g oil)
			Free acid	Combined acid	Peroxide	Alcohol	Carbonyl	H_2O	CO_2	Volatile acids	
40 V.I.* California	150	2826	5·0	11·0	—	2·9	1·5	36	21·0	2·4	135
50 V.I. California	150	3010	4·5	10·0	0	8·9	8·9	51	26·0	2·0	100
60 V.I. California	150	2853	4·7	12·0	0	2·5	1·4	56	12·0	1·7	65
70 V.I. California	150	2800	4·1	9·0	0	0·4	1·2	68	9·2	1·6	25
80 V.I. California	150	2803	3·8	10·0	0	0·6	—	60	16·0	1·4	6
85 V.I. California	150	2800	4·1	12·0	—	1·3	2·5	65	16·0	1·2	2
Mid-Continent neutral	150	3233	4·5	12·0	0·1	0·7	5·0	49	—	1·1	—
Synthetic oil made from cracked wax olefins	150	2532	5·9	16·0	1·0	9·0	9·0	34	7·0	2·4	0
	110	2980	6·6	15·0	0·4	8·0	19·0	26	4·9	3·8	0
White oil	110	1571	13·0	19·0	5·0	13·0	44·0	11	—	1·3	0

* V.I. refers to viscosity index as defined by Dean and Davis.

Tertiary > Secondary of ethyl group > Secondary of nucleus > Primary . . . . (4)

The carbon atoms in the *cyclo*hexane ring are not attacked with equal facility, those adjacent to the ethyl group being more readily attacked.

Waters has shown that the mechanism of breakdown of the hydroperoxide is conditioned by the presence of acids, bases, and metals, so that the initial free radical mechanism may change in the course of the reaction as a result of the formation of acidic products or by the solution of metals. Frank has discussed this problem in some detail.

The subsequent course of the reaction is therefore to some extent dependent upon the products of oxidation. In the case of a single hydrocarbon this leads to a complex of reaction products, but in the case of mixtures of hydrocarbons the effect of the oxidation products of one hydrocarbon upon the rate and extent of oxidation of another is unpredictable. Some indication of the type of oxidation products obtained from various hydrocarbons is given in Tables I and II

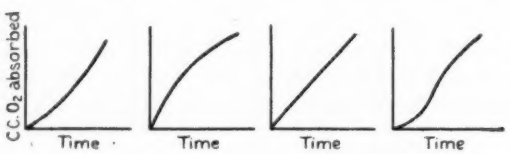


FIG 1 FIG 2 FIG 3 FIG 4

THE LOW TEMPERATURE LIQUID PHASE OXIDATION OF HYDROCARBONS

(Stephens [17] and Larsen [27]). In addition to the products given in Table II, Larsen found that aromatic hydrocarbons give condensation products which precipitate out as sludge if the oxidation is continued for a sufficient length of time. The variation in the type of oxidation product obtained from mixtures of hydrocarbons is illustrated in Table III (Larsen) for the oxidation at 150° C of a variety of lubricating oils. The variation in carbonyl and asphaltene content in the various oils is particularly noteworthy. Analysis of the oxidation products is a difficult procedure, and the results obtained do not give a great deal of information concerning the mechanism of the primary reaction. The rate at which the hydrocarbon absorbs oxygen—under conditions in which the availability of oxygen is unlimited—gives a somewhat better picture of the type of reaction. Figs 1–4 illustrate the various types of curve which may be obtained. These curves are: (i) auto-catalytic; (ii) auto-retardant; (iii) linear; and (iv) initially auto-catalytic followed by auto-retardant. Obviously other combinations can be obtained, and in the early stages at least the catalysed autoxidation of 2,5-dimethylhexane gives a curve which is auto-catalytic followed by linear leading to auto-retardant, the linear stage being normally that of maximum oxidation rate.

TABLE IV

Oxidation Rates of Pure Hydrocarbons

Data from Larsen, Thorpe, and Armfield.

Hydrocarbon	Oxidation temp, °C	Time to absorb 2000 cc of O_2 per gram-mol, hours	Type of curve (see Fig 1)
1. Tetralin	100	1·5	2
2. Tetra*iso*butylene	110	2	3
3. Octahydroanthracene	110	2	4
4. 9,10-Dihydro-9,10-di-*iso*butylanthracene	110	2·5	2
5. *n*-Octadecylbenzene	110	2·5	3
6. *β*-*n*-Octadecyltetralin	110	3·5	4
7. Poly*iso*butylene $(C_4H_8)_{12}$	110	4	3
8. α-Phenyl-Δ^1-tetralybutane	110	7	4
9. 9,10-Di-*iso*butylperhydroanthracene	110	7	1
10. 5-*iso*Butylacenaphthene	110	8	2
11. *n*-Hexadecylbenzene	110	12	4
12. Perhydroanthracene	110	12	1
13. Hydropoly*iso*butylene $(C_4H_{10})_{12}$	110	17	4
14. Hexaethylbenzene	110	23	1
15. *β*-*n*-Octadecyldecalin	110	24	1
16. Fluorene	110	26	2
17. Decalin	110	27	1
18. Di*cyclo*hexyl	110	28	1
19. *n*-Amyl*cyclo*pentane	110	28	1
20. *n*-Amylbenzene	110	28	3
21. 1-α-Naphthyl-1-*n*-butylhexadecene	150	2	3
22. *n*-Octadecyl*cyclo*hexane	110	37	1
23. *n*-Hexadecyl*cyclo*hexane	110	45	1
24. Cetane	110	45	1
25. *n*-Decane	110	47	1
26. *sec*-Amylbenzene	110	68	1
27. *tert*-Amylbenzene	110	85	1
28. Benzylnaphthalene	110	120	3
29. Diphenylmethane	110	70	2
30. Di-α-naphthylmethane	150	12	1
31. α-*n*-Octadecylnaphthalene	150	33	1
32. Poly-*sec*-amylnaphthalene	150	42	1
33. α-*iso*Amylnaphthalene	150	55	2
34. α-Methylnaphthalene	150	62	2
35. Di-*sec*-amylnaphthalene	150	72	3
36. *β*-*sec*-Amylnaphthalene	150	140	1
37. *β*-Methylnaphthalene	150	150	3
38. *tert*-Butylnaphthalene	150	150	3
39. Naphthalene	150	150	3

Tables I–IV and Figs. 1–4 are taken from the paper by Zuidema, H. H., *Chem. Rev.*, 1946, 38, 197.

Table IV gives the results obtained by Larsen, and since these results have been discussed at a considerable length by Zuidema, it will suffice to note here that paraffins, naphthenes, and alkylnaphthenes (*i.e.* fully hydrogenated compounds) are the most stable and have auto-catalytic absorption curves (types 1 or 4), whilst olefins, partially hydrogenated condensed rings, and benzene derivatives containing a long side chain are the least stable and do not in general give an auto-catalytic curve.

More recent work by Booser and Fenske [28] is illustrated in Figs 5–7, in which the rate of oxidation of a series of hydrocarbons and some mixtures, alone and in the presence of metallic copper, and at several temperatures, is given. Figs 5 and 6 are of interest in showing that mixtures of hydrocarbons do not absorb oxygen in a predictable manner. Thus Fig 5 gives results obtained with a mixture of hexadecane and *cis*-decalin compared with the oxidation rates of the pure hydrocarbons under similar conditions. In this case the mixture oxidizes at the same rate as the

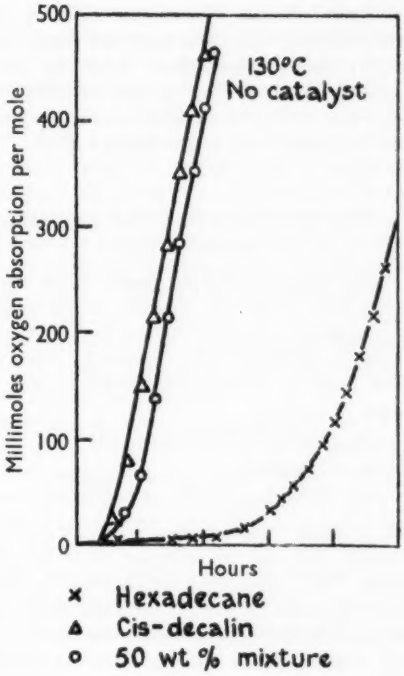


Fig 5

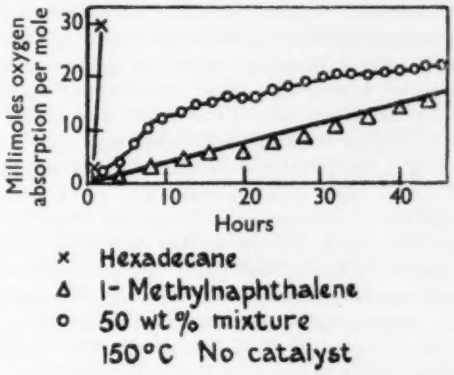


Fig 8

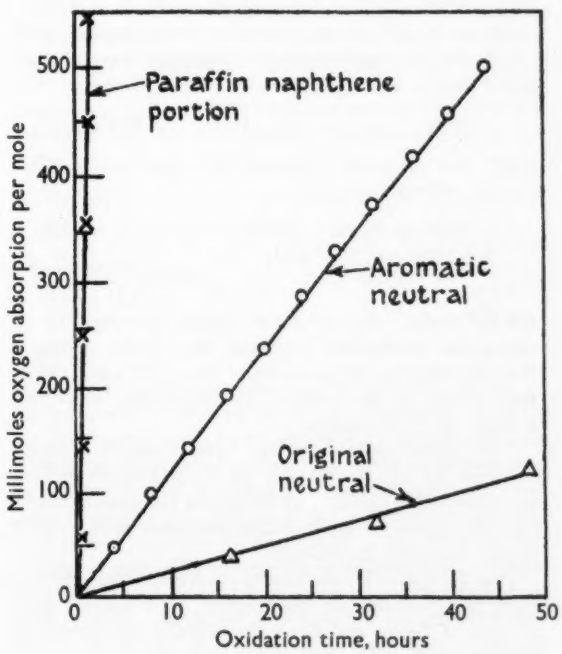


Fig 7

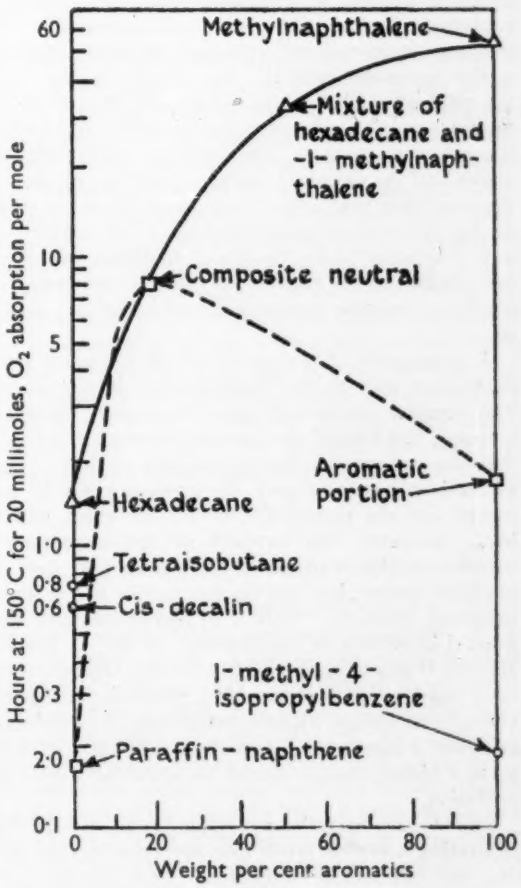


Fig 6

Figs 5–8 are taken from the paper by Booser, E. R., and Fenske, M. R., *Industr. Engng Chem.*, 1952, **44**, 1850.

pure *cis*-decalin, suggesting that the more readily oxidized hydrocarbon is preferentially attacked in the mixture. Fig 6, however, shows the behaviour of a mixture of hexadecane and 1-methylnaphthalene. Here the oxidation rate of the mixture is similar to that of the pure 1-methylnaphthalene and very much slower than the rate for the oxidation of hexadecane alone. The slow rate of oxidation of 1-methylnaphthalene is believed to be due to the formation of α-naphthol, which inhibits further oxidation, so that the inhibiting effect is observed in mixtures containing this and similar hydrocarbons. A further illustration of the unpredictable character of the oxidation of mixtures is shown in Fig 7. Here the rate of oxidation of a neutral fraction of Pennsylvania oil is compared with the rate of oxidation of the paraffin–naphthene portion and aromatic portion of the same oil separated by silica gel. The original neutral oil is oxidized more slowly than either of the constituent fractions. Despite the greater stability of the aromatic portion as compared with the paraffin–naphthene portion, there were indications that the aromatic hydrocarbons were preferentially oxidized in the composite neutral. The results suggest that the original neutral contained an inhibitor which is removed by silica gel absorption and is not eluted with the aromatic portion. The relatively high sulphur content of the aromatic fraction, however, precludes the possibility that sulphur compounds in the original neutral oil are the oxidation inhibitors. It would have been interesting to see the rate of oxidation curves for the mixture of the paraffin–naphthene and aromatic fractions in similar proportions to the original neutral oil.

A comparison of the nature of the oxidation products from each of the three fractions is of interest. The original neutral oil gave the lowest viscosity increase, but formed the greatest amount of surface deposits and gave a highly coloured product. The aromatic concentrate gave the greatest viscosity increase, and the highest *iso*pentane-insolubles, and a black product. The product of the naphthene–paraffin portion was almost colourless and free of insoluble matter, but was the most acidic of the three oxidation products. This is in agreement with the general behaviour of transformer oils for, as Wood-Mallock [29] has shown, a highly refined aromatic-free oil is readily oxidized to acidic products, but gives virtually no sludge, whilst a less refined oil containing aromatic hydrocarbons is less readily oxidized but gives a higher sludge content for a similar degree of oxidation.

Jezl [30] has recently extended these results by separating a typical crude into saturates and mono-, di-, and tri-nuclear aromatics. The sulphur and nitrogen components were previously removed. The four fractions and combinations of them were examined in an oxygen-uptake apparatus. The greater part of the oxidation occurred in the saturated fraction when the fractions were examined separately, but recombination with the aromatics substantially reduced the oxygen uptake. Unfortunately, here again the oxidation of the original oil was not compared with the recombined oil.

THE INITIATION STEP IN THE REACTION

Previous mention has been made of the suggestion of George and Robertson that the initial step in the reaction sequence involves energy chains rather than free radicals, whilst Waters,[19] Ivanov,[31] etc., support the view that the activation results in free radical formation.

Waters, *et al.* $RH \xrightarrow{\text{activation}} R\cdot + (H\cdot)$ . . (1)

George and Robertson

$$RH \longrightarrow R^*H \longrightarrow R^* \quad . \quad . \quad . \quad (2)$$

Neither of these suggestions is entirely satisfactory, particularly for the uncatalysed, low temperature oxidation. An alternative suggestion is that the reaction is initiated by oxygen, and that in the absence of catalysts and at temperatures below those necessary for the decomposition of the hydroperoxide thus formed, the reaction stops at this stage. The reaction might conceivably proceed by one of several different mechanisms. The first, and most probable, is that oxygen in solution in the liquid hydrocarbon first combines with a hydrogen atom, breaking the C–H bond, and the two radicals so formed immediately unite to give the hydroperoxide

$$R\cdot H + O_2 \longrightarrow R\cdot + HO_2\cdot \longrightarrow ROOH \quad (5)$$

Uri [32] has proposed initiation by way of a cobalt–oxygen–solvent complex.

$$Co^{++} + O_2 \longrightarrow Co^{++}O_2\cdot \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$Co^{++}O_2 + (Co^{++}XH) \longrightarrow Co^{++} + Co^{+++}X^- + HO_2\cdot \quad . \quad . \quad (7)$$

Alternatively, the reaction might proceed by a molecular mechanism in which the oxygen molecule first attacks the carbon atom of the C–H bond which, particularly in the tertiary hydrocarbons, will carry a slight negative charge.

This latter mechanism has been thought unlikely in view of the formation of α-methylenic hydroperoxides from olefins. A molecular reaction followed by rearrangement, such as that proposed by Kenner,[24] would, however, be possible.

It is conceivable that traces of olefin in the reaction medium could initiate the reaction by a scheme such as that of Bawn and Sharp,[33] whereby an extremely reactive carbonium radical is produced.

$$R^1R^2C = CHR^3 + Co^{+++} \longrightarrow Co^{++} + R^1R^2\dot{C} - \overset{+}{C}HR^3 \quad . \quad (8)$$

There is no direct experimental evidence which can be claimed to support any of these mechanisms, but it may be argued that since the energy required to break a C–H bond is approximately 95 k.cal/mol for a primary, 89 k.cal/mol for a secondary, and 86 k.cal/mol for a tertiary bond, it is difficult to explain the large differences in the case of tertiary and secondary C–H bonds if the proposals of Waters or George and Robertson are accepted. Of the alternative mechanisms, the energy required for reaction (5) could in part be supplied by the formation of the $(HO_2)\cdot$ radical since $H\cdot + O_2 \longrightarrow (HO_2)\cdot$ is exothermic with a heat of reaction of −46 k.cal/mol. If the reaction is of the molecular type, the energy requirements of the reaction are likely to be much lower than required for the breaking of the C–H bond.

Irrespective of the mechanism of the initiation reaction, the available evidence suggests that in the absence of catalysts and at temperatures at which the hydroperoxide is stable, the oxidation of hydrocarbons proceeds slowly to the formation of a hydroperoxide and appears to stop at this point. The chain reaction by which the oxidation proceeds further and with auto-catalytic character involves the breakdown of the hydroperoxide and the formation of free radicals.

PROPAGATION OF THE REACTION

The hydrogen bromide catalysed gas phase oxidation of hydrocarbons leads to the formation of hydroperoxides at temperatures some 40°–50° C lower than that needed for the normal oxidation.[34] The initiating step is considered to be the formation of a bromine atom which acts essentially as a free radical in the subsequent propagation steps:

Initiation—

$$HBr + O_2 \longrightarrow Br\cdot + HO_2\cdot + 39{\cdot}4\ \text{k.cal/mol} \quad (9.1)$$

Chain sequence—

$$Br\cdot + HR \longrightarrow HBr + R\cdot \quad (9.2)$$
$$R\cdot + O_2 \longrightarrow RO_2\cdot \quad (9.3)$$
$$RO_2\cdot + HBr \longrightarrow ROOH + Br\cdot \quad (9.4)$$

In this reaction sequence the peroxy radical is immediately converted to the hydroperoxide, which at the conditions of the reaction is stable and can therefore be isolated. Reactive hydroperoxides can be prepared in this manner. This confirms the view that the further oxidation of the hydrocarbon beyond the peroxide stage is essentially a function of the peroxy radical and not of the hydroperoxide. Ubbelohde [35] considers that the failure of attempts to cross the reaction chain of hydrocarbon oxidation with those of acetaldehyde, and the fact that oxidation chains initiated by bombardment with hydrogen atoms (Badin [36]) stop at the stage of ketone production, is explained by the fact that the temperatures at which these experiments were conducted are too low to permit the chain-multiplying process

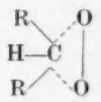
$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot \quad (10)$$

From a general consideration of the reactions Ubbelohde suggests that the peroxy radicals $RO_2\cdot$ can store excess vibrational energy for a considerable period and "that a critical step in hydrocarbon oxidation arises from the fact that the radical RO_2^* must endure a comparatively large number of collisions before it can complete the process

$$RO_2^* + RH \longrightarrow ROOH + R\cdot \quad (11)$$

with eventual chain multiplication."

A further suggestion made by Ubbelohde is that the peroxy radical may act either as the straight chain $R\cdot CH_2\cdot O\cdot O\cdot$ or as the (electron deficient) peroxide radical



Reactions of the first form ($R\cdot CH_2\cdot O\cdot O\cdot$) will lead to the hydroperoxide, whereas reactions in the second form may lead to alkoxy-peroxides (derivatives of aldehydes and hydrogen peroxide) such as were found by Mondain-Monval and Quanquin [37] in the uncatalysed oxidation of normal paraffins at 300° C. Despite the general similarity between liquid phase oxidation and low temperature (250°–300° C.) gas phase oxidation of hydrocarbons there is a growing body of evidence to suggest that the two mechanisms are essentially different and that the difference may well lie in the manner in which the peroxy radical breaks down. By analogy there may be a change in reaction mechanism in the liquid phase reaction if the temperature at which the accelerated catalysed oxidation is carried out exceeds the thermal decomposition temperature of the hydroperoxide.

SOLUBLE METAL SALTS

It is now well established that certain metals, notably copper, cobalt, iron, and manganese in the soluble state (usually added as the naphthenate or stearate), catalysed the liquid phase oxidation of hydrocarbons in that they reduce the length of the induction period although they do not appear to affect the maximum rate of oxidation. The end of the induction period usually coincides with the change of the state of the metal ion from a lower to a higher valency state and, in the case of cobalt for instance, this can be followed by the change in colour from the cobaltous (pink Co^{++}) to the cobaltic (green Co^{+++}) ion. In the experiments described by Wibaut [38] the green colour persists for some time, the rate of oxygen

absorption remaining constant, but finally the red colour of the cobaltous ion reappears, the rate of oxygen absorption decreases, and the catalyst flocculates. Similar observations have been made by Bawn [39] and other workers.

Wibaut has made a careful study of the kinetics of the cobalt stearate catalysed oxidation of many hydrocarbons and has proposed the following scheme in the case of the oxidation of 2-methylheptane, which is in general agreement with that proposed earlier by Waters, George, and Robertson, and more recently by Bawn. It will be noted that the catalyst sequence of $m^{++} \longrightarrow m^{+++} \longrightarrow m^{++} \longrightarrow m^{+++}$, etc., is maintained by reactions (1) and (3).

Initiating reaction—

$$\mathrm{ROOH} + m^{++} \longrightarrow \mathrm{RO}\cdot + m^{+++} + \mathrm{OH}^- \quad . \quad (12.1)$$

$$\mathrm{ROOH} \longrightarrow \mathrm{ROO}^- + \mathrm{H}^+ \quad . \quad . \quad . \quad (12.2)$$

$$\mathrm{ROO}^- + m^{+++} \longrightarrow \mathrm{ROO}\cdot + m^{++} \quad (12.3)$$

$$\mathrm{RO}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R}\cdot \quad . \quad . \quad (12.4)$$

Propagating reaction—

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{ROO}\cdot \quad . \quad . \quad . \quad . \quad . \quad (12.5)$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}\cdot \quad . \quad (12.6)$$

Terminating reaction—

$$2\mathrm{ROO}\cdot \longrightarrow \mathrm{ROOR} + \mathrm{O_2} \quad . \quad . \quad . \quad (12.7)$$

$$\mathrm{RO}\cdot \longrightarrow r\cdot + (\mathrm{CH_3})_2\mathrm{C{=}O} \quad . \quad . \quad (12.8)$$

Side reaction—

$$r\cdot + \mathrm{O_2} \longrightarrow r\mathrm{OO}\cdot \quad . \quad . \quad . \quad . \quad . \quad (12.9)$$

$$r\mathrm{OO}\cdot + \mathrm{RH} \longrightarrow r\mathrm{OOH} + \mathrm{R}\cdot \quad . \quad (12.10)$$

$$r\mathrm{OOH} \longrightarrow \text{Inactive products.} \quad . \quad (12.11)$$

$\mathrm{RH} = (\mathrm{CH_2})_2{\cdot}\mathrm{CH}{\cdot}\mathrm{CH_2CH_2CH_2CH_2CH_3}$

$\mathrm{R}\cdot = (\mathrm{CH_3})_2{\cdot}\mathrm{CCH_2CH_2CH_2CH_2CH_3}$

$r\cdot = {\cdot}\mathrm{CH_2CH_2CH_2CH_2CH_3}$

m^{++}, m^{+++} = Metal ions of the catalyst

Kinetic analysis of this reaction scheme shows that the reaction rate is dependent upon hydrocarbon and catalyst concentrations, but is independent of oxygen pressure. At low concentrations of oxygen a further step must be introduced, namely, the reaction $\mathrm{R}\cdot + \mathrm{ROO}\cdot \longrightarrow \mathrm{ROOR}$, which then makes the reaction dependent upon oxygen concentration, but this reaction is unlikely at the high oxygen concentrations under which various kinetic studies have been made.

Normally the induction period observed with soluble metal catalysed oxidations is ascribed to the necessity of oxidizing the metal ion. The oxidizing agent is believed to be the hydroperoxide as in the reaction

$$\mathrm{ROOH} + m^{++} \longrightarrow m^{+++} + \mathrm{RO}\cdot + \mathrm{OH}^- \text{ or } \mathrm{RO}^- + {\cdot}\mathrm{OH} \quad (13)$$

If the hydrocarbon contains hydroperoxide at the commencement of the reaction, then it might be expected that the induction period would be shortened, and this is in fact the case. Presumably the metal ion does not catalyse the initial formation of the hydroperoxide but catalyses the overall oxidation by facilitating the breakdown of the hydroperoxide and the initiation of a free radical chain mechanism.

CATALYSIS BY A METALLIC SURFACE

The mechanism of the copper-catalysed oxidation of insulating oils is discussed by Thompson [40] in this symposium.

Although many investigations have been reported upon the effect of various metal surfaces on mixed hydrocarbons, such as lubricating oils or transformer oils, the mechanism by which the metal enters into the oxidation reaction has not hitherto been extensively studied. In general, it is assumed that the metal enters into solution in the oil, first by action of hydroperoxide (weak acids) and then subsequently, at an increasing rate, by action of acidic degradation products. Once in solution in the oil the metal acts as a soluble metal catalyst and finally precipitates in the sludge.

The mechanism by which metallic copper catalyses the oxidation of hydrocarbons must, in the first instance, depend upon the character of the metal surface and secondly upon the facility with which metallic ions can be transferred from such a surface into the oil. It is generally accepted that copper forms an oxide film with great rapidity, and the continued growth of this film requires that metallic ions can pass outwards.[41] The rate of oxidation (of copper) follows a parabolic law

$$x^2 = K_1 t + K_2 \quad . \quad . \quad . \quad (14)$$

where x = the film thickness and t = time. It has been shown [42] that K_1 can be predicted from the ionic and electronic conductivities of the oxide layer. On copper a film of "$\mathrm{Cu_2O}$" actually contains $\mathrm{Cu^+}$, $\mathrm{Cu^{++}}$, and electrons in the lattice, and it is probable that such a surface could accept additional electrons on certain sites of low electron density. At low temperatures, especially if the film is very thin, Mott [43] has suggested that the oxidation is due to a quantum mechanical "tunnel" effect.

Current theories concerning the building of the oxide film on a copper surface indicate that the metal surface can in fact accept electrons even through an oxide film and that the reaction by which the metal removes an electron from a C–H bond is possible.

$$\mathrm{RH} + \mathrm{Cu^{++}} \longrightarrow \mathrm{R}\cdot + \mathrm{H^+} + \mathrm{Cu^+} \quad (15)$$

Moreover, there is a certain amount of evidence to suggest that metallic ions can in fact move into the surface film. In aqueous solutions of hydroxy-acids (tartaric, citric, and the like) copper ions pass readily

from the metal surface into complex anions in solution, far more readily in fact than nickel, although the electrolytic solution pressure of nickel is far greater than that of copper.[44]

It may not be necessary, however, to postulate that the copper surface does in fact accept an electron from a C–H bond. If the metal surface is in contact with a hydrocarbon which is capable of forming a hydroperoxide, then two competing reactions are possible in the presence of oxygen, *i.e.* the formation of an oxide film on the copper and the formation of the hydroperoxide of the hydrocarbon. Provided the oxygen has to diffuse through the hydrocarbon, it is reasonable to assume that some hydroperoxide will be formed and that the subsequent reaction will involve, at least in part, reaction between the hydroperoxide and the metallic ion.

If this is the case, then the reactions (12.1) and (12.3)

$$R{\cdot}OOH + m^{++} \longrightarrow RO{\cdot} + m^{+++} + OH^- \quad . \quad (12.1)$$

$$ROO^- + m^{+++} \longrightarrow ROO{\cdot} + m^{++} \quad . \quad (12.3)$$

by which the catalyst " chain " is maintained take place at the metal surface. Moreover, provided that the oxygen required for reaction (12.5) ($R{\cdot} + O_2 \longrightarrow ROO{\cdot}$) is available at the metal surface, the whole of the proposed initiating and chain propagation reactions can occur at the metal surface without the metal ion entering into solution. The result of such a sequence of reactions would be a marked increase in the peroxide content of the oil. As the peroxide content increases, the possibility of a breakdown of the peroxide also increases, and this breakdown now offers a second series of reactions in which oxygen is consumed, namely, the oxidation of the breakdown products to ketones and acids. Under conditions of limited availability of oxygen (Massey [45]; Garner and Wilson [46]) this second series of reactions, coupled with the breakdown of the hydroperoxides, results in a decrease in the peroxide content of the oil, accompanied by increase in the acidity.

At this stage in the reaction sequence the metal ion begins to pass into the oil phase. In the experiments of Garner and Wilson [46] the metal (lead) first gained weight and then progressively lost weight, with the appearance of a cloudy precipitate in the oil, the lead appearing as a complex hydroxy organic lead salt and not as lead oxide. This suggests that the first step in the reaction is the formation of an insoluble lead salt on the metal surface which is subsequently dislodged by further action on the metal surface. Obviously the nature of such a product will depend upon the character of the hydrocarbon oxidation product and the metal. Copper readily forms complex coordination compounds with hydroxy organic acids, suggesting that the copper ion passes into the oil phase as a complex. Such a complex would aggregate and form sludge. Analyses of transformer oil sludges, although showing that metals are present, and that the metals are associated with organic acids and hydroxy acids, do not give any clear picture as to the manner in which the metal ion is bound.

Waters [47] suggests that the cobalt-catalysed oxidation of olefins proceeds by way of a complex as in the following sequence

$$Co^{+++} + nRH \longrightarrow \text{Complex} + Co^{++} + \text{Product} \quad . \quad (16)$$

Bawn [48] states " ions of cobalt and other transition elements do exist as complex ions in solution " and that in the presence of water the cobalt may well act as ($Co^{+++}H_2O$) which may aggregate to form insoluble complexes.

These findings, together with those of Wibaut,[38] Bawn,[39] and Garner and Wilson,[46] make it not unreasonable to suppose that copper exists in oils as a complex which loses its catalytic power through its aggregation into a hydrated gel micelle. Steric factors may cause the loss of catalytic effect.

It is of some importance to establish whether or not the metal ion actually passes into solution in the oil phase. If it does not the reaction remains a heterogeneous catalytic reaction throughout, whereas if the copper dissolves in the oil phase the reaction becomes a homogeneous catalytic reaction. Beaven, Irving, and Thompson [49] quote results of Larsen suggesting that the oxidation of oils in the presence of copper is a homogeneous reaction, and state therefore that " the effectiveness of the catalyst must depend primarily upon its rate of dissolution into the oil (presumably by reaction with acids)." The statement by Massey,[45] however, that in all cases examined by him filtered transformer oils did not contain detectable amounts of soluble copper supports the alternative view that the copper complex, except in unusual circumstances, remains insoluble in the oil phase. The occasional appearance of green oils in transformer windings is attributed by Massey to unusual conditions of restricted availability of oxygen. Irving and Thompson,[50] however, state that many transformer oils when oxidized under the conditions of the IP 56 oxidation test (catalysed solid copper foil) were found to contain " significant amounts of chemically combined copper (of the order of 50 p.p.m. of oil), in the form of salts and organic complexes." Both groups of workers, however, agree that when a soluble copper salt is used in accelerated oxidation tests the amount of soluble copper is very quickly reduced to around 5 p.p.m. and remains substantially constant thereafter.

Raab [51] describes how several oils were tested in transformers in service and also in standard IEC accelerated aging tests using both soluble copper and solid copper catalysts. Some evidence is given that with certain American oils solid copper catalysts

might yield results correlating better with service than results with soluble catalysts.

This difference in correlation may be due to variation in the nature of the hydrocarbon oil, but is more reasonably assumed to be the difference which might be expected in a heterogeneous reaction in which, under certain conditions, the rate of diffusion of oxygen through the liquid to the solid surface becomes the rate-determining step, whereas in conditions of excess oxygen chemical reactions occurring at the surface may control the subsequent behaviour of the copper ion. For several reasons it is believed probable that the oxidation processes occurring in the transformer do in fact take place at the surface of the copper and that the subsequent course of the reaction depends upon the rate at which oxygen can be made available. It is of interest to consider from this viewpoint the statement of Salomon [52] that there is a certain periodicity in the deposition of sludge, which Salomon attributes to the successive oxidation of complexes. Assuming that the first reaction is the breakdown of peroxides at the copper surface, the oxygen content at the metal–oil interface would quickly be reduced and further oxidation of the oil, now catalysed by peroxy radicals, would occur at some distance from this interface. In the absence of oxygen at the interface the copper may now be attacked by acid oxidation products giving a soluble copper salt which diffuses outwards into the oil phase. Because the catalytic activity of the soluble copper salt is much greater than that of the copper surface, the subsequent oxidation of the oil is essentially catalysed by this copper salt and not by the surface until, by processes which render the copper salt insoluble, this is precipitated. Assuming the ideal case that all the soluble copper ions are precipitated and in the sludge form do not possess catalytic activity, the rate of sludge formation will now fall or cease completely until the oxygen can diffuse to the metal–oil interface and set up anew the series of reactions leading afresh to oxidation of the oil, solubilizing of the copper, oxidation in the presence of soluble copper salt, and again sludge formation. Such a sequence of reactions is, of course, possible only if the rate at which the oxygen diffuses into the oil is less than the rate at which it is consumed in the oxidation reactions, and this would not be the case in any of the accelerated oxidation tests in which oxygen is bubbled through the oil. The Weiss–Salomon test, however, relies upon diffusion through the air–oil interface, and represents conditions of limited oxygen availability.

CATALYSTS OTHER THAN METALS

The discussion has so far been limited to the case of metal catalysts, and particularly to that of copper. Although there is evidence that many other types of material can in fact act as catalysts in the oxidation of oils (*cf.* Massey), the work reported on such materials is difficult to correlate except in a general sense, as Massey has done. The important group of materials used to provide a protective coating to the copper coils of the transformer, namely varnishes, lacquers, paper insulation, fibres, etc., are subject to considerable variation in character, and if properly prepared and correctly "baked out," etc., appear to provide satisfactory protection against oil deterioration. Massey gives a great deal of information on tests of such materials, and points out that the results show a widely erratic behaviour. This, particularly in relation to the varnishes, is almost certainly due to the difficulty of obtaining uniform surface conditions and an equivalent degree of permeability. Broadly speaking, however, the effect of such materials on peroxide and acidity development is much lower than that of copper, but they may contribute on occasion to sludge formation. This effect is, however, unlikely to be permanently renewable, as is the copper surface, and the study of transformer service behaviour by Gossling and Welch [53] indicates that after the initial deterioration of an oil its replacement by new oil may in fact remove the "acidity accelerator." Obviously the presence of unsaturated hydrocarbons will provide a point of oxidation attack leading to hydroperoxides and subsequent catalysing of the oxidation of the oil. If such compounds are adequately polymerized they prove a satisfactory protective covering of the copper surface.

OXIDATION PRODUCTS

Oxidation products, particularly acids and sludge, are related to the nature of the oil undergoing oxidation, the type of catalyst employed, the temperature at which the oxidation is conducted, and the degree of availability of oxygen. The work of Larsen, quoted earlier in this review, shows the marked influence of the nature of the oil on the asphaltene content of oxidized oil, but the effect on the combined acids is relatively small. There is, however, a marked difference in the rate at which acidity develops, and this is in some way related to the ability of the oil to form sludge under the conditions of test. The differences between oils of increasing degree of refining has been amply demonstrated, and it is now accepted that oils which have been excessively refined develop acidity without the formation of sludge, whereas oils still retaining some of the aromatic hydrocarbons have a greater stability towards acidity, but do develop some sludge. Presumably this is related to the fact that certain of the products of oxidation of aromatic hydrocarbons, *e.g.* phenols, are oxidation inhibitors, but it is also due to the greater ease of oxidation of the aromatic hydrocarbons, resulting in oxidative-con-

densation reactions which effectively use up the available oxygen before it can accomplish the breakdown of the carbon chain to a carboxyl group.

There are other factors which from time to time have been considered of importance in relation to sludge formation and which are difficult to assess from a study of literature. For instance, Stadnikov *et al.*[54] claimed that sludges were formed by condensation of resinous substances with the oxidation products of the oil, catalysed by sodium sulphonates left in the refined oil as a result of insufficient washing after oleum treatment.

Boisselet and Mouratoff[55] considered that their analysis of transformer sludges showed the sludge to contain only acids and metallic soaps, and suggested that the acids were cyclic saturated acids, not sulphonic acids. Much later Kreulen and Kreulen van Selms[56] described the precipitated "resins" as "predominantly carbonyl containing hydroxy acids and their anhydrides." From the early work of Rodman[57] to the present day the complexity of the sludge has defied a rational approach to the mechanism of its formation. It is, however, now well established that certain aromatic hydrocarbons, such as *iso*propylbenzene and *p*-cymene, can undergo oxidative condensation at their boiling point to form dimers and higher molecular weight polymers, by chain mechanisms involving the peroxy radical, in which the point of attack and of subsequent dimerization is the tertiary carbon atom. These polymer products are probably still capable of further oxidation, although this has not been demonstrated. The building up of high molecular weight structures is at least feasible, and the subsequent oxidation of these molecules could produce the hydroxy acids of unknown structure which figure so prominently in the literature.

The complexity of these sludges suggest that no single entity is involved in their formation and that no single reaction mechanism can explain their occurrence at any given stage in the oxidation. Their properties and mode of occurrence do not preclude the possibility that they are formed first by a hydrated metal complex adsorbing high molecular weight organic molecules to form a stable colloidal system which gradually gels as the acidity of the oil increases.

OXIDATION INHIBITORS

The problem of protecting mineral oils in service by the addition of anti-oxidants has been discussed by many authors and is outside the scope of this review. An excellent survey has been given by Thompson[58] and Evans,[65] and extensive lists of inhibitors have been made by several authors; Rosenwald *et al.*,[59] Bolland and ten Have,[60] Lowry *et al.*,[61] and Calhoun.[62] Some measure of relative efficiencies is given, but these have been determined from laboratory tests, which may not accord with service conditions.

The mechanism by which the common amino and phenolic inhibitors act has been studied extensively in recent years. Pedersen[63] lists four possible mechanisms.

(1) Donating a hydrogen atom to the chain-carrying peroxy radical.
(2) Donating an electron to the chain-carrying peroxy radical.
(3) Addition to the peroxy radical before or after being itself partially oxidized.
(4) Some mechanism, as yet not known, may occur which does not involve the peroxy radical.

The peroxy radical is converted into a molecule which cannot participate further in the oxidation sequence. When the inhibitor has been destroyed by oxidation the oil will be then oxidized, and the oxygen-uptake curve which follows is then the same as that which would have occurred had no inhibitor been added in the first place.

The oxidized inhibitor molecule or radical appears in some cases to be capable of further inhibition. Kooyan and Bickel,[64] investigating a pure hydrocarbon, have found kinetic agreement with the following scheme:

$$ArXH + RO_2\cdot \longrightarrow ArX\cdot + ROOH \quad . \quad (17)$$
$$ArX\cdot + RO_2\cdot \longrightarrow \text{Stable products} \quad . \quad (18)$$

The stable products are stated to be adducts. Primary amines, possessing two replaceable hydrogen atoms, are therefore capable of inactivating two peroxy radicals by hydrogen donation, and of inactivating a further peroxy radical by the formation of a stable adduct.

If the mechanism by which the inhibitor acts is as above, it is unlikely that the efficiency of inhibitors of this type could be materially increased. There is therefore considerable interest in the development of a catalytic method of peroxide decomposition, or in a self-regenerating inhibitor which might form an adduct with the peroxide, and subsequently decompose into inert derivatives of the peroxy radical while the inhibitor itself is regenerated.

CONCLUSIONS

The discussion has been confined to the mechanism of the oxidation of mineral oils and the breakdown of transformer oils by oxidation. Only brief mention has been made of inhibitors and inhibited oils and the difficulties associated with the development of internationally acceptable methods of testing both inhibited and uninhibited oils. It is clear, however, that certain important aspects of the oxidation of

mineral oils require elucidation, and several of the papers presented in this symposium report the results of a co-operative research programme organized by Panel E/Ad of the Electrical Research Association in the universities and in industrial laboratories.

Much of the work is concerned with the mechanism of the metal-catalysed reaction and has an important bearing upon the use of soluble metal catalysts in accelerated ageing tests.

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ERA/IEC WORK ON OXIDATION TESTS FOR INSULATING OILS IN THE LAST DECADE *

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SUMMARY

With the continued use of widely differing national oxidation test methods for transformer oils, a considerable effort is worthwhile in the attempt to secure international agreement upon one method. The British collaborative work to this end is summarized. The possibility of the replacement of metallic by soluble metal catalyst has been investigated. The need to obtain more fundamental knowledge of the mechanisms involved has become evident, and the activities of the ERA in this direction are reported.

INTRODUCTION

At the symposium on insulating oils held by the IP in 1946 the pre-war work of ERA for IEC was shown to be leading to proposals for an improved British specification for transformer oil.[1] The suggested measurement of the acidity developed in the sludge test was adopted by BSI in the 1951 version of B.S. 148. With the closer specification of the condensation temperature for the effluent vapours during the test, also proposed at the symposium, and the subsequent introduction of *n*-heptane as sludge precipitant, the test does not now seem to invoke the serious criticism with regard to its precision which was offered against it in 1946.

The oils distributed in Great Britain to the present standard appear to be accepted in general as giving satisfactory service. Without doubt this has been helped by a greater consciousness of the limitations of oil on the part of the user, so that, by regular inspection and attention to oil cleaning when necessary, the avoidance of contamination of new oil by oxidized material, and the general improvement of servicing methods, the conditions of operation tended for a while to become somewhat less onerous. In the transformer the practice of painting all iron surfaces with oil-resistant anti-corrosive paint became general, and doubtless the oil benefited. More recently, however, the electrical industry has tended to adopt, where possible, systems of "temperature loading" in order to make the best economic use of plant within the restrictions of the heat stability of the cellulosic insulation, and the resultant operating conditions are considerably more arduous for the oil.

In its more severe form this trend is being looked after by the use of oxidation-inhibited oil, but there is clearly room for investigations leading to a better understanding of the fundamental processes involved in transformer oil oxidation, which might result in further improvements in oil quality. Alternatively, such studies may point the way to possible improvements in operating conditions, by the elimination of practices which are undesirable in their effects upon oil.

In ERA work in the last decade collaboration in IEC programmes has again played a large part, and this has been found to combine usefully with the ERA work in its major aims as mentioned in the previous paragraph. The present review cannot include detailed references to all the work which has been carried out, and the emphasis will be upon work from which has developed the present trends of thought in ERA, in particular that leading to some of the work separately reported in this symposium.

IEC Technical Committee No. 10 reunited at Stresa in 1949 under the chairmanship of Professor Weiss of France and, the broad principles for an international oxidation test having been laid down, a Permanent Sub-Committee was formed to organize international co-operative work. A report of the Sub-Committee was made in 1954 and published in the following year.[2] It contains the original Stresa terms of reference and summarizes the results of four years' work leading to the proposal of a specified type of apparatus and test procedure. Agreement is recorded upon a tentative "selection method" for new oils, using copper wire catalyst at a temperature of 100° C, with passage through the oil of oxygen at a rate of 1 litre per hour. The duration of the test is 164 hours, but it is acknowledged that, in the opinion of at least some members, this does not satisfy the original terms of reference for the duration of the test to be as short as possible. Work with this aim using soluble catalysts is reported, this being claimed by some to result also in improved precision. In the discussions which followed the report the continuation of the work of the Sub-Committee with soluble catalyst was agreed. Further, the possibility was suggested of shortening the test duration by raising the temperature to 110° C without the introduction thereby of reaction processes which are radically different from those occurring in service. These points are discussed in more detail later in this paper.

Although soluble catalysts had been used in earlier

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studies of the oxidation of lubricating oils, the emphasis upon their special suitability for transformer oils is due to H. Liander of Sweden, who gave a paper [3] on this subject to the 1948 session of C.I.G.R.E.* Inevitably this had a considerable influence upon the discussions at the Stresa IEC meeting in the following year and, thereafter, upon the direction of IEC work.

The Liander method required the simplest of apparatus, oxygen being blown into the oil in test tubes without condensers, so that its further study was readily embraced in the IEC decision that its first work would be an investigation of the adaption of ASTM D670–42T, Method A, to its requirements.

THE STRESA PROGRAMME—1949

The Permanent Sub-Committee decided that the temperature of 120° C of the ASTM test would be retained, but that oxygen would be blown over the oil surface at 1 litre per hour instead of air at a $\frac{1}{2}$ litre per hour. It was agreed also to make the alternative trial of blowing oxygen through the oil instead of over the surface. The catalytic effect of the standard copper wire would be compared with that of soluble copper introduced at a concentration of 100 p.p.m. of metal, and it was later agreed to include also soluble iron.

The delegates of Belgium, France, Great Britain, Holland, Italy, Sweden, Switzerland, and the U.S.A. would each distribute a sample of oil considered to be representative of that generally used in his country. In addition to the work summarized above, each delegate would carry out tests on all the oils by his normal national method and also by his normal method modified by the use of soluble copper as catalyst.

The soluble catalysts would be introduced as copper and iron naphthenates, standardized solutions of which had been made by the Shell Petroleum Co. Ltd for use by Liander. These same solutions have since been used throughout the international work.

It was early agreed to use *n*-heptane as precipitant for sludge because of its convenient availability in most countries in a closely standardized form as a reference fuel for octane number determination.

In the following year it was decided to include in the programme six "Insulating Reference Oils" which had been prepared for experimental work by the Shell Petroleum Co. Ltd. These had been specially selected to include oils which were respectively more highly and less refined than were currently normal in Great Britain, so providing a range of aromaticity. A description of these oils is given in another contribution to the present symposium.[5]

As was customary, BSI delegated the investigations in Great Britain to ERA. The experimental work in this first programme was carried out in the laboratories of W. B. Dick & Co. Ltd and at the Thornton Research Centre of the Shell Petroleum Co. Ltd, and was completed by 1951.

The oxidation test results obtained upon the "national" oils by the standard British method are shown in Table I, in which the results are given in some detail for the purpose of illustrating the precision obtainable after the modifications introduced in 1951, even prior to the introduction of *n*-heptane as sludge precipitant. The mean values given exclude any results outside the current limits for repeatability ("test results shall not differ from the mean by more than 10 per cent"). The tests so excluded are shown in parentheses and amount to three only in a total of forty tests carried out. The reproducibility is seen to have been reasonably good.

TABLE I

National Oils—Standard B.S. 148 Oxidation Test (Identical with IP 56)

Oil Ref.	Sludge formation, %					Acidity development, mg KOH/gm				
	Lab. X		Lab. Y		Overall mean	Lab. X		Lab. Y		Overall mean
	Test result	Mean	Test result	Mean		Test result	Mean	Test result	Mean	
A	1·20 1·23	1·22	1·20 1·25 1·10	1·18	1·20	2·35 2·68	2·52	1·80 1·75 1·60	1·72	2·04
B	0·85 1·02	0·94	0·97 1·09	1·03	0·99	2·64 2·94	2·79	2·40 2·55	2·48	2·64
C	0·75 0·73	0·74	1·12 0·99 1·09 (0·91)	1·07	0·94	1·30 1·47	1·39	1·95 1·75 1·80 1·70	1·83	1·66
D	1·00 1·09	1·05	1·03 1·11	1·07	1·06	1·51 1·65	1·58	1·40 1·45	1·43	1·50
E	0·67 0·66	0·67	0·93 0·77	0·85	0·76	1·09 1·01	1·05	1·10 0·95	1·03	1·04
F	0·66 0·61 0·62 (0·85)	0·63	0·87 0·87	0·87	0·73	1·47 2·01 2·01 1·83	1·83	1·70 1·70	1·70	1·79
G	1·18 1·08 1·06 (1·41)	1·11	1·12 1·13 1·16 1·24	1·16	1·14	3·60 2·39 2·27 3·66	2·75	2·15 2·15 2·25 2·50	2·26	2·62
GB	0·76 0·79	0·78	0·93 0·82	0·88	0·83	1·43 1·43	1·43	1·50 1·40	1·45	1·44

The British National Oil Sample is denoted by the reference "GB," all other "national" oils being given arbitrary reference letters.

No precision limits for the acidity of the oxidized oil are laid down for the standard method, and it is evident from the results given in Table I that at the time of this work neither the repeatability nor the reproducibility of acidity development was as good as would be wished.

Five of the "national" oils were found to meet

* Liander and his co-worker, Ericson, reported [4] their more recent work in this field at the ASTM symposium on insulating oils held in 1954.

the then current requirements of B.S. 148 (maximum sludge 1·1 per cent,* maximum acidity 2·5 mg KOH/g), while three failed. Although the failures were marginal, the further work in this programme suggests that they were significant.

When the British method was modified by the replacement of the standard copper foil catalyst by 100 p.p.m. of soluble copper, the degree of oxidation was in general higher (Table II), although not to the degree which had been expected from consideration of Liander's earlier work. It appeared from this that the stronger catalytic effect of the soluble copper was not so pronounced at 150° C as at 120° C. An outstanding feature of this part of the work was the great improvement in precision, the agreement between results being remarkably good for an oxidation test. There seemed by inspection only minor correlation between the sludge values and those obtained in the standard test, but on acidity development the ordinal ratings of the oils were closely similar for the two methods. No further work was carried out by this modification of the British test because it seemed important at the time not to deviate from collaboration in the general trend of the IEC work, in connexion with which there had been wide expression of opinion that test temperatures should not exceed 120° C.

TABLE II

Modified B.S. 148 Test using Copper Naphthenate as Catalyst (100 p.p.m. Copper)

Oil Ref.	Sludge formation, %			Acidity development, mg KOH/g			Standard method (metallic copper)	
	Test result		Mean	Test result		Mean	Overall mean results	
	Lab. X	Lab. Y		Lab. X	Lab. Y		Sludge	Acidity
A	—	1·31 1·25	1·28	—	2·45	2·45	1·20	2·04
B	0·96 0·93	—	0·95	4·20 4·41	—	4·31	0·99	2·64
C	—	1·27 1·33	1·30	—	2·60 2·65	2·63	0·94	1·66
D	1·17 1·18	—	1·18	2·64 2·64	—	2·64	1·06	1·50
E	1·05 1·04	—	1·05	1·97 1·93	—	1·95	0·76	1·04
F	1·05 1·01	—	1·03	3·48 3·24	—	3·36	0·73	1·79
G	1·37 1·29 1·47 1·36	1·21	1·34	4·62 4·54 5·16 4·83	3·25	4·48	1·14	2·62
GB	1·04 1·07	1·29 1·18	1·15	2·40 2·52	3·15 3·10	2·80	0·83	1·44
IRO 1	1·26 1·20	—	1·23	1·85 2·02	—	1·94	1·27	1·81
IRO 2	1·39 1·40	—	1·40	1·97 2·06	—	2·02	1·36	1·73
IRO 3	0·62 0·66	—	0·64	4·33 4·54	—	4·44	0·63	4·53
IRO 4	0·86 0·81	—	0·84	3·64 3·62	—	3·58	1·18	2·94
IRO 5	1·31 1·27	—	1·29	2·77 2·90	—	2·84	0·93	1·50
IRO 6	0·70 0·67	—	0·69	4·54 4·50	—	4·52	0·66	4·07

In the agreed programme with the modified ASTM method the precision, especially the reproducibility, was poor throughout. Thus, the tests for a duration of 72 hours with solid copper catalyst were duplicated in the two British laboratories and, considering the overall averages of the test results of twelve oils separately in each laboratory, the ratios of these averages were 1·81 for sludge formation and 1·30 for acidity development. This was typical also of results with soluble catalyst and, with the experimental conditions used at this stage of the work, no marked difference was evident in the precision obtainable with soluble compared with metallic catalyst.

Despite the poor precision, it was possible to draw some general conclusions upon the oxidation properties of the Insulating Reference Oils when tested at 120° C with metallic copper catalyst:

1. The most highly refined oils I.R.O. 3 and 6 each gave several times more sludge, and many times more acidity, than any other oil.
2. I.R.O. 5, described as a normal transformer oil, gave the lowest sludge and acidity of any oil.
3. While I.R.O. 2 and 4 gave very little more sludge than I.R.O. 5 and, in the case of I.R.O. 2, not a great deal more acidity, the acidity formation of I.R.O. 4 was markedly more than I.R.O. 5. It is to be noted that I.R.O. 2 and 4 are distinguished in chemical type from I.R.O. 5 in having respectively higher and lower aromatic contents.
4. The sludge formation of I.R.O. 1, the solvent-refined feedstock, was fairly markedly higher than I.R.O. 2, 4, and 5, and its acidity development greater than for I.R.O. 2 and 5, but not greatly different from I.R.O. 4.

It will be seen from Table II that only I.R.O. 5 conforms with B.S. 148 : 1951.

The results with the "national" oils may be summarized as falling within the limits formed by the group of I.R.O. 2, 4, and 5, with several oils closely similar to I.R.O. 5.

With regard to the intensity of the catalytic action, it was clear that metallic copper was considerably weaker than soluble copper or soluble iron. Some

* The subsequent adjustment of the maximum allowable sludge to 1·2 per cent was consequent upon the introduction of *n*-heptane as precipitant.

X

oils appeared more susceptible to soluble copper than to soluble iron, but, on the whole, the latter was the more active.

The longest tests with soluble catalysts were for 48 hours and, compared with metallic copper at this duration, the tests with soluble catalysts showed on the average about five times more sludge and three times more acidity.

Supplementing the agreed programme, it was at this time (early 1951) that the Shell Thornton Research Centre began its work upon copper dissolution from metallic copper catalyst, the more recent work upon which is the subject of a separate paper [5] in this series.

At a meeting of the Permanent Sub-Committee at Stockholm in 1951 the international results with the modified ASTM method were also found to show poor precision, there being three- and four-fold differences between laboratories. Considering the results of the tests in which oxygen gas was merely blown upon the oil surface, it was concluded that the poor precision was due mainly to the poor standardization of the availability of oxygen and of the degree of scavenging of volatile oxidation products. However, in the tests in which oxygen was bubbled through the oil at a temperature of 120° C, in the absence of a condenser, certain national oils suffered unduly high oil losses by volatilization. It was specially desired to keep the apparatus simple, avoiding if possible the use of a condenser; accordingly, it was agreed for further work to bubble oxygen through the oil but to lower the test temperature to 100° C.

It was clear that the use of soluble catalysts at the high concentration of 100 p.p.m. tended to mask the very large differences between certain of the oils which had been brought to light in the tests with metallic copper. Further, such a concentration of soluble catalyst was felt by some members to be too far removed from those found in oils in service, upon which, however, there was available at that time very little definite information.

T. Salomon, the member for France, brought forward evidence that a substantial proportion of the "sludge" was derived from the decomposition of the copper and iron naphthenates rather than from oil oxidation. The measurement and analysis of the ashes of sludge, which had been included in much of the work, although not with sufficiently good precision in the earlier stages to allow any very definite conclusions to be drawn, was later developed into a potent tool for studying the mechanism of the oxidation processes.[5]

THE STOCKHOLM PROGRAMME—1951

After considerable discussion, a concentration of 10 p.p.m. of soluble copper or iron, or of 5 p.p.m. of each of these together, was agreed for further work, with a test temperature of 100° C. These catalysts would be compared with metallic copper in the form of the standard ASTM wire, and with iron wire to be supplied from Sweden.

It was realized that these changes would necessitate longer test durations for reasonably high final degrees of oil deterioration. In order to acquire information upon precision it was decided that all laboratories would carry out tests for a fixed duration, which was agreed at 164 hours. However, since some delegates felt it desirable for the sludge and acidity at the end of the tests to correspond approximately with those often attained in service before oils were considered unfit for further use, it was left with members to explore the effect of test duration in a more general way. In the course of this work information would also be obtained upon the variability of merit ratings of oils at different test durations.

More closely defined experimental conditions were agreed, for example with regard to the apparatus dimensions, the sludge precipitation conditions, and the method for acidity measurement. Particular attention was given to the standardization of the venting of the tubes.

In the ERA work in this programme the two laboratories already mentioned were joined by those of Lobitos Oilfields Ltd and Manchester Oil Refinery Ltd, the catalytic conditions being divided for exploration.

Part of the British work was completed in time for informal discussion at a meeting in Paris in 1952, by which time it was seen that the iron wire had negligible catalytic effect in tests at 100° C up to 164 hours, except for I.R.O. 3 and 6. After 308 hours I.R.O. 4 and three of the "national" oils were showing a slight development of acidity, but still negligible sludge. It was soon decided to allow work with this catalyst to lapse.

At this meeting the difficulties in several countries with the determination of the acidity of the oxidized oil were discussed, and it was agreed to use in the meantime both IP Method 1-A, carried out directly on the *n*-heptane solution after sludge precipitation, and IP Method 1-B on the residual oil freed from solvent by distillation.

The ERA group accordingly embarked upon correlation work in the four laboratories, to compare results by the two IP methods, ASTM D974–51T, ASTM D664–51 (electrometric method), a fluorescent indicator method, and two European methods similar to IP Method 1-A but with different benzene to alcohol ratios. Results were obtained on four oxidized oils with and without prior distillation of the *n*-heptane solvent. The reproducibility was in no case found to be good, and, finally, the recommendation was made to IEC to use IP Method 1-A direct upon the *n*-heptane solution. Several other national

bodies concurred as a result of their own trials. This method remains standard for IEC work on insulating oils, excepting that, following reports from several countries in 1956 that more precise results were obtainable with the use of alcoholic instead of aqueous alkali solution for titration, it has been agreed that the former would be adopted for future work. The decision has been made by the IP to make a similar change in the 1958 version of the method.

In the British work upon the new programme of oxidation tests at 100° C the repeatability was found to be reasonable, but the reproducibility, in the limited amount of work carried out in more than one laboratory, was not as good as could be wished.

With metallic copper as catalyst, tests were made for 164 and 332 hours. For the Insulating Reference Oils, the separation into two types was in good agreement with the previous work at 120° C, but the differentiation was now more strongly marked. The eight " national " oils all fell approximately within the values found for I.R.O. 2 and 5, and were therefore clearly distinguished from under- and over-refined types. It was, however, evident that a test of 164 hours duration as a minimum would be required in order to obtain degrees of deterioration of magnitudes convenient for measurement.

With soluble iron and with soluble copper (10 p.p.m.) durations of 44, 92, and 164 hours were used. Excluding the highly refined oils I.R.O. 3 and 6, the degree of oxidation attained in 44 hours with soluble catalyst was of similar general order to that in 164 hours with metallic copper. (Averages for 12 oils: sludge with metallic copper, soluble copper, soluble iron—0·07, 0·05, 0·06 per cent, acidity—0·30, 0·41, 0·36 mg KOH/g.)

With 10 p.p.m. soluble iron, the differentiation of the under-refined oil I.R.O. 1 and the highly refined oils I.R.O. 3, 4, and 6, from the medium refined oils I.R.O. 2 and 5 was clearly marked, as were the tendencies towards respectively high acidity and high sludge development which had been shown by two of the " national " oils with metallic copper.

In the case of 10 p.p.m. soluble copper the I.R.O. 1 and 4 were not so clearly distinguished from I.R.O. 2 and 5, and some of the " national " oils deteriorated a little more than any of these four reference oils.

With few exceptions the fourteen oils were tested with mixed soluble copper and iron (5 p.p.m. of each) for 44, 68, 164, and 308 hours, while for three oils the duration was extended to 620 hours. The extents of oxidation in 44 hours were similar to those with the separate soluble catalysts, but the differences between the reference oil types were perhaps slightly accentuated.

The differences between the " national " oils were in many cases quite small, so that the direct comparison of the ordinal ratings under the several catalytic conditions would constitute a rather too strict test of correlation. A more reasonable test in this regard is obtainable from the results of the division of the eight oils into groups of the respectively greater and less stable four oils:

Number of oils in common with the four oils in the less stable group for metallic copper	Sludge	Acidity
164 hour test duration at 100°C throughout		
Soluble copper, 10 p.p.m.	3	3
Soluble iron, 10 p.p.m.	3	2
Soluble copper, 5 p.p.m. + soluble iron, 5 p.p.m.	4	4

With a reasonably promising test technique now in sight it became important to consider closely the precision obtainable, especially as information had become available that ASTM were abandoning the use of the " sludge accumulation test," ASTM D670–42T Method A, owing to its poor precision, which was reported to be in the case of repeatability 33·5 per cent, and of reproducibility 53 per cent.

Accordingly, Professor Weiss in early 1953 requested the British group, with its organization as a number of separate laboratories operating cohesively through the ERA, to undertake a programme expressly designed to provide data for a statistical analysis. Liander had recently reported work showing that the use of mixed soluble copper and iron at a concentration of 20 p.p.m. of each, at a temperature of 100° C, resulted in a degree of oxidation adequate for measurement in a test duration of only 48 hours. A programme of identical tests was therefore agreed to be carried out in each of the four laboratories already mentioned with the addition of the Metropolitan-Vickers Electrical Co. Ltd.

The following test conditions were used:

Temperature	100°C
Catalyst	20 p.p.m. copper plus 20 p.p.m. iron added as naphthenates
Duration of tests	24, 48, and 72 hours
Three tests at each duration—a pair of tests being carried out together and a single test at another time	
Acidity measured by IP Method 1-A, and by ASTM D974–51T, without prior distillation of solvent	
Oils tested	I.R.O. 1, 3, and 5, and three selected " national " oils

Substantial degrees of oxidation were attained in the tests of 24 hours duration, but the very large differences previously obtained between I.R.O. 3 and the other oils tended to be developed only in the 48- and 72-hour tests. The results for I.R.O. 1 are given in Table III, which shows that the precision attained, as judged by inspection, was of a high order. A similar high standard of precision was reached with all oils excepting I.R.O. 3, of which the degree of oxidation measured either as sludge or acidity was fifteen to twenty times greater than for any of the other five oils.

TABLE III

Insulating Reference Oil 1

Catalyst: 20 p.p.m. Cu + 20 p.p.m. Fe as naphthenates.
Temperature: 100° C

Laboratory	Sludge, %	Acidity	
		(*a*) IP	(*b*) ASTM
Test duration: 24 hours			
A	0·53 0·55 0·50	2·02 1·80 1·57	2·47 2·20 2·02
Mean	0·53	1·80	2·23
B	0·56 0·55 0·60	1·59 1·66 1·59	1·84 1·84 1·84
Mean	0·57	1·61	1·84
C	0·61 0·60 0·58	1·9 1·8 1·9	1·7 1·7 2·0
Mean	0·60	1·9	1·8
D	0·60 0·56 0·52	1·95 1·80 1·80	2·00 1·70 1·75
Mean	0·56	1·85	1·82
E	0·61 0·65 0·63 0·64	1·57 1·57 1·55 1·68	2·24 2·13 2·13 2·02
Mean	0·64	1·59	2·13
Test duration: 48 hours			
A	0·87 0·96 0·85	1·57 1·80 1·80	2·02 2·24 2·24
Mean	0·89	1·72	2·17
B	0·98 0·96 0·91	1·94 1·87 1·69	1·97 1·72 2·08
Mean	0·95	1·83	1·92
C	0·96 0·98 0·87	2·5 2·3 2·4	2·2 2·1 2·0
Mean	0·94	2·4	2·1
D	0·86 0·95 0·73	1·70 1·90 1·65	2·00 2·00 1·85
Mean	0·85	1·75	1·95
E	0·95 0·97 1·01	1·68 1·68 1·57	2·24 2·22 2·00
Mean	0·98	1·64	2·15
Test duration: 72 hours			
A	1·11 1·17 0·99	1·80 1·80 1·57	2·24 2·24 1·80
Mean	1·09	1·72	2·09
B	1·08 0·89 1·11	1·56 1·54 1·70	1·97 1·97 2·05
Mean	1·03	1·60	2·00
C	1·19 1·19 1·15	2·5 2·5 2·6	2·2 2·0 2·3
Mean	1·18	2·5	2·2
D	1·19 1·19 1·14	1·90 1·90 1·95	2·00 2·00 2·00
Mean	1·17	1·92	2·00
E	1·18 1·18 1·25	1·79 1·68 1·79	2·02 2·02 2·12
Mean	1·20	1·75	2·05

The test results were statistically analysed for precision at the British Electricity Authority Research Laboratories, Leatherhead.

Excluding I.R.O. 3, which is in any case not a transformer oil of modern type, the averages of the repeatabilities and reproducibilities for sludge formation in the remaining oils were:

	24 hours	48 hours	72 hours
Repeatability, % variation from the mean . . .	23·0	18·3	16·4
Reproducibility, % variation from the mean . . .	34·1	28·1	26·7

These estimates of precision were calculated upon the basis that the mean value $\pm(3 \times$ standard deviation) will include 99·7 per cent of all the readings, and accordingly they represent comparatively high precision values for an oxidation test.

It was clear from an inspection of the results that the degree of oxidation was increasing rapidly with time only up to the 24 hours duration, so that the precision improved as the oxidation curve flattened with the longer durations.

At a meeting of the Permanent Sub-Committee at Windsor in 1953 the work from several countries in the Stockholm programme was seen to allow generally similar conclusions to be drawn to those discussed above for the British group, but the principle of the use of soluble catalysts was not yet acceptable to all. There was complete agreement that, with copper wire catalyst, the procedure which had been developed provided the basis for a satisfactory test if a duration of 164 hours at 100° C were acceptable.

The reproducibility shown in the international results was far from good. This is evident from Table IV, which summarizes the average results of all countries which reported, the highest and lowest results also being shown. However, as stated in the introduction to this paper, it was decided to recommend to the parent Committee that details of the

TABLE IV

International Results for Metallic Copper Catalyst in Stockholm Programme (Nine Laboratories)

164 hours at 100°C.

Oil Ref.	Sludge formation, %			Acidity, mgKOH/g		
	Mean	Lowest	Highest	Mean	Lowest	Highest
A	0·076	0·039	0·10	0·40	0·28	0·62
B	0·067	0·04	0·095	0·36	0·20	0·56
C	0·029	0·009	0·06	0·21	0·16	0·29
D	0·034	0·02	0·045	0·26	0·16	0·40
E	0·064	0·056	0·09	0·28	0·19	0·50
F	0·030	0·01	0·043	0·25	0·11	0·43
G	0·094	0·076	0·109	0·46	0·21	0·78
GB	0·044	0·022	0·07	0·28	0·18	0·49
IRO 1	0·221	0·13	0·37	0·75	0·56	0·84
IRO 2	0·084	0·03	0·211	0·27	0·13	0·35
IRO 3	8·77	6·38	12·61	15·97	6·69	20·2
IRO 4	0·072	0·05	0·09	0·75	0·28	0·98
IRO 5	0·020	0·01	0·029	0·11	0·07	0·18
IRO 6	10·01	5·9	12·22	17·16	14·92	~20

method be published,[2] the aim being to encourage its wider use in the expectation that the precision would improve as experience was gained. This recommendation was accepted at a plenary session of IEC Technical Committee No. 10 held in Paris in 1954.

The British view, and that of several other countries, was that a test of 164 hours duration was rather long, not satisfying the terms of reference given in this regard at Stresa. This conclusion was confirmed in discussions by BSI Committee ELE/20, which is responsible for the British method. A method requiring nine days for completion, instead of four days by the existing method, was viewed with disfavour by the oil industry, and several members representing users also held the view that a test of this duration would be justifiable only if it were shown that oils of improved quality would be ensured, which was not apparent in the work. However, the advantages of an international test were recognized, and it was decided to continue work with modifications of the IEC test aiming at a shorter duration. Accordingly, no further international programme having been laid down, ERA from 1953 onwards continued work independently, the same five laboratories collaborating.

It has been shown above that one way of obtaining a test of reasonably short duration, at a temperature of 100° C, is by the increase of soluble catalyst concentration, *e.g.* to 20 p.p.m. copper plus 20 p.p.m. iron. However, it was found in a close study of the results then available with these conditions that a loss of sensitivity resulted, compared with either metallic copper or with soluble catalyst at a total concentration of 10 p.p.m.

At the Windsor meeting of the Sub-Committee one member of the British group had reported that with 2 p.p.m. copper plus 2 p.p.m. iron at 120°C, in ASTM tubes with condensers added, several of the I.R.O. and "national" oils were oxidized in only 24 hours to extents, speaking generally, between those for copper wire and 10 p.p.m. soluble copper in 164 hours. It was, however, desired to avoid the complication of the use of condensers.

It was clearly advisable to investigate more thoroughly the possibility of increasing the temperature to 110° C, without adding condensers, and keeping the soluble catalyst concentration at 10 p.p.m. or lower. It was felt, too, that their application at low concentrations would render soluble catalysts less liable to criticism on the grounds of departure from conditions occurring in the field. At the same time, it was now seen that a temperature of 110° C was not above that likely to occur at least for short periods in certain zones of transformers in the most modern trends of practice.

Accordingly, after making some exploratory tests in 1953 with I.R.O. 1 and 5, the group of five British laboratories began in 1954 a programme of tests of 48 hours duration at 110° C, using otherwise the IEC technique which had by then been agreed for publication. The oils used were I.R.O. 1, 2, 4, and 5, and the catalytic conditions as follows:

(1) 5 p.p.m. copper plus 5 p.p.m. iron as soluble naphthenates;

(2) 2 p.p.m. copper plus 2 p.p.m. iron as soluble naphthenates;

(3) Copper wire with 2 p.p.m. copper plus 2 p.p.m. iron as soluble naphthenates;

(4) Copper wire.

A summary of the results of this work is given in Table V, in juxtaposition to certain others of relevance.

It is evident that, speaking generally, the extent of oxidation in the tests for 48 hours at 110° C with any of the catalytic conditions (1) to (4) is within the range of those shown by the international results for

TABLE V

IEC Tests Carried Out at 110° C. Test Duration—48 hours. Average Results of Five Laboratories for Catalytic Conditions (1), (2), *and* (3).

S = Sludge, %. A = Acidity, mg KOH/g.

Catalyst	Insulating Reference Oil							
	No. 1		No. 2		No. 4		No. 5	
	S	A	S	A	S	A	S	A
(1) 5 p.p.m. copper + 5 p.p.m. iron	0·46	0·93	0·24	0·50	0·26	2·12	0·12	0·48
(2) 2 p.p.m. copper + 2 p.p.m. iron	0·22	0·70	0·11	0·33	0·11	1·16	0·04	0·23
(3) Copper wire with 2 p.p.m. copper + 2 p.p.m. iron	0·28	0·82	0·16	0·43	0·17	1·77	0·08	0·40
(4) Copper wire. One laboratory only	0·15	0·80	0·10	0·87	0·08	1·90	0·04	0·40
(1a) as (1). Earlier work. Mean of 36 results in 3 British laboratories	0·50	1·00	—	—	—	—	0·11	0·41
Comparative international mean values for 164 hours at 100° C:								
10 p.p.m. copper	0·20	0·70	0·17	0·45	0·14	1·05	0·12	0·41
5 p.p.m. copper + 5 p.p.m. iron	0·51	1·00	0·30	0·61	0·20	1·11	0·11	0·40
Copper wire	0·22	0·75	0·08	0·27	0·07	0·75	0·02	0·11

164 hours at 100° C, which have been accepted as being of adequate magnitude for accurate measurement.

With regard to correlation, Table VI gives the ordinal ratings with all the variations of conditions reported in Table V. The precision of the tests not having yet been established, those adjacent oils are bracketed together where the test results, either for sludge or acidity, differ by no more than 10 per cent of the greater result. The 10 per cent is arbitrarily chosen, but its use helps to bring into a better perspective the minor failures of correlation.

It may be concluded from this work that there is a good possibility of a satisfactory test of short dura-

tion at a temperature of 110° C, using either metallic copper or mixed soluble copper and iron catalyst. In considering the correlation in the results with various catalysts it is not to be overlooked that the Insulating Reference Oils used in this work yield considerably larger differences in test results than occur with normal transformer oils, especially those conforming

TABLE VI

Ordinal Ratings of I.R.O. 1, 2, 4, and 5 with the Variations of Conditions as Reported in Table V

	Temperature: 100°C Duration: 164 hours			Temperature: 110°C Duration: 48 hours			
	Catalyst			Catalyst			
	Copper wire	10 p.p.m. copper	5 p.p.m. copper + 5 p.p.m. iron	Copper wire	5 p.p.m. copper + 5 p.p.m. iron	2 p.p.m. copper + 2 p.p.m. iron	2 p.p.m. copper + 2 p.p.m. iron + copper wire
Sludge	5	5	5	5	5	5	5
	4	4	4	4	2	4	2
	2	2	2	2	4	2	4
	1	1	1	1	1	1	1
Acidity	5	5	5	5	5	5	5
	2	2	2	1	2	2	2
	4	1	1	2	1	1	1
	1	4	4	4	4	4	4

Those adjacent oils are bracketed together where the test results, either for sludge or acidity, differ by not more than 10 per cent of the greater result.

with B.S. 148. Similar studies were therefore started in ERA using a group of representative British transformer oils. However, this work was not brought to a point at which conclusions could be drawn because it had become evident in the meantime that there had occurred, throughout the work at 110° C, a loss of the good reproducibility hitherto shown in the British work.

The collaborating laboratories accordingly then engaged upon systematic studies of the test conditions in an endeavour to find a cause for the poorer precision, focusing attention especially upon the conditions above oil level which might affect the degree of loss of volatile products, but no satisfactory solution was obtained. However, as a result, certain refinements of the testing procedure were proposed to IEC in 1956.

The importance of accurate dosage of soluble catalysts at the low concentrations now in use was realized, and some work to examine the effects of minor variations of concentration was started. This merged into part of a more fundamental study of the mechanism of the catalytic processes occurring, which is reported in detail in another paper [5] in this symposium. It was at this time felt that, with the limited resources engaged, it would be better to concentrate upon such studies of the mechanism rather than to continue the search, in however systematic a manner, for conditions which would give adequate precision.

The evidence of a rather satisfactory correlation between tests with metallic copper and the mixed soluble catalysts in low proportions has been examined separately [6, 11] by van Rysselberge, the Chairman of the Belgian National Committee and Secretary of the IEC Committee No. 10. Based upon the average international results at 100° C for 164 hours, and the British results at 110° C for 48 hours as quoted above, he draws similar conclusions to those foregoing; but having extended the work to include three commercial transformer oils of types not very different from I.R.O. 2 and 5, he does not find their ordinal merit ratings with metallic copper identical with those for 5 p.p.m. soluble copper plus 5 p.p.m. soluble iron.

However, the present writer would comment that, the precision of the test not yet being established, the differences in the test values of the three oils may not be significant. It is to be noted that van Rysselberge concludes with a recommendation that the test temperature of 110° C be adopted in the IEC method.

THE CASE FOR SOLUBLE CATALYSTS IN TRANSFORMER OIL OXIDATION TESTS

A discussion of the use of soluble catalysts instead of the conventional copper metal has been provided elsewhere [4] by Liander and Ericson, so no attempt is made here to do more than mention a few relevant points.

Initially the attraction of laboratory workers to soluble catalysts was largely based upon the hope that they might provide a better means of standardization of catalytic activities than was provided by metallic copper surfaces. It had for long been felt that one reason for the generally poor precision of oxidation tests using metallic copper rested in the difficulty of obtaining metallurgically and chemically identical surfaces. Work carried out in the U.S.A. to provide information upon the relative precisions of the IEC method with metallic copper and soluble catalysts has been summarized by Raab,[12] the conclusion being given that the " spread " of test values is greater when soluble catalysts are used. The overall levels of these results were, however, higher, and the view of the group forming ERA Section E is that coefficients of variation are better parameters of precision in such tests. Accordingly, in a written contribution to the discussion of the ASTM symposium, the author has drawn attention to the fact that the *percentage* spread of results for sludge is without exception very much smaller with soluble catalysts than with solid copper.

It may be mentioned in the foregoing connexion that two memoranda dealing with the statistical analysis of oxidation test results have in recent years been submitted by ERA to ASTM through the medium

of IEC. For the preparation of these ERA is indebted to C. N. Thompson and his statistician colleagues on the staff of "Shell" Research Ltd.

TABLE VII

Copper and Iron Contents of Used Transformer Oils

Data submitted by Central Electricity Authority Research Laboratories			Data submitted by Manchester Oil Refinery Ltd	
Age of oil, years	Iron content, p.p.m.	Acidity mgKOH/g	Copper content, p.p.m.	Acidity, mgKOH/g
1·0	0·2	<0·02	0·14	0·01
1·0	0·1	0·02	0·35	0·02
1·0	0·2	<0·02	0·18	0·02
1·5	0·1	0·07	0·70	0·02
3·0	0·8	0·06	0·15	0·03
3·0	3·6	0·13	0·28	0·04
3·0	3·3	0·07	0·20	0·04
3·0	0·1	0·12	0·12	0·04
3·0	0·4	0·31	0·33	0·04
3·0	0·5	0·09	0·28	0·07
5·0	0·2	0·07	0·15	0·07
5·0	2·1	0·07	0·19	0·07
5·0	0·1	0·16	0·36	0·07
5·0	0·9	0·10	0·49	0·07
5·0	0·3	0·04	0·74	0·07
5·3	2·7	0·13	0·16	0·09
7·0	1·6	0·33	0·25	0·11
7·0	3·0	0·20	0·50	0·11
7·8	0·3	0·18	0·32	0·13
8·0	0·7	0·06	0·25	0·13
8·0	1·3	0·25	0·22	0·16
9·0	1·4	0·02	0·22	0·16
10·0	0·5	0·04	0·22	0·18
10·0	0·2	0·06	0·11	0·20
10·0	0·5	0·22	0·38	0·22
10·0	1·0	0·19	0·59	0·22
10·0	0·3	0·07	0·17	0·23
10·0	0·1	0·20	2·8	0·23
10·0	0·3	<0·07	0·12	0·24
11·0	0·9	0·14	0·15	0·29
11·0	0·3	0·07	0·55	0·29
12·0	0·3	0·24	0·27	0·31
12·0	0·4	0·22	0·21	0·31
12·0	0·8	0·65	0·26	0·31
15·0	0·3	0·14	5·8	0·32
17·0	0·8	0·16	0·36	0·34
17·5	0·3	0·27	0·34	0·36
18·0	0·3	0·54	0·28	0·45
18·0	0·5	0·37	0·33	0·45
18·0	0·6	0·10	0·28	0·47
19·0	0·3	0·11	0·33	0·49
20·0	0·4	0·18	1·04	0·49
20·0	0·0	0·19	0·36	0·54
20·0	1·3	0·14	0·55	0·69
20·0	0·4	0·12	0·18	0·99
20·0	2·4	0·17	0·26	1·80
20·0	6·6	0·21	1·28	2·18
20·0	0·7	0·35	4·70	2·34
20·0	1·1	0·22		
20·5	0·6	0·19		
21·0	0·2	0·27		
21·0	0·2	0·11		
22·0	1·0	0·18		
22·0	2·7	0·20		
24·0	1·6	0·75		

With regard to the justification of the principle of the use of soluble catalysts in transformer oil oxidation tests instead of the usual metallic copper, it had been known for a long time that oils in service were often found to contain copper and iron in solution, but the extent was not satisfactorily known. Accordingly, two members of the British group made available the information given in Table VII. All analyses had been carried out on clear oil samples free from suspended or settled solid matter. The results show no definite correlation between either iron content or copper content and acidity. Most of the dissolved metal contents are relatively low, *i.e.* under one p.p.m., but each series includes examples of oils with high metal contents. Thus, in the list of copper contents there are two in the region of 5 p.p.m. while eight of the iron contents are above 2 p.p.m., the highest being 6·6 p.p.m. These data were made available to IEC at the 1956 meeting, and the opinion was offered that they supported the view that the use of soluble catalysts in oxidation tests for transformer oils, at the lower concentration levels under consideration, represented no wide departure from conditions existing in practice.

Soluble catalysts have manifest advantages in the design of tests for inhibited oils, as has, for example, been shown in a proposal [13] by Irving and Bravey to assess these by the IEC method using 20 p.p.m. copper plus 20 p.p.m. iron at a temperature of 110° C. ERA has, so far, not engaged upon the development of oxidation test methods for inhibited transformer oils.

That aspect of the case for use of soluble catalyst which is dependent upon a satisfactory correlation of the ordinal merit ratings with those for metallic copper has been discussed earlier, but it is also dealt with in much detail in another paper to this symposium.[5] The conclusion is there reached "that it is evident that suitable concentrations of soluble catalysts will correctly rate the oxidation characteristics of oils."

INVESTIGATIONS WITH ASTM HIGH PRESSURE OXIDATION BOMB

A further section of IEC work which has been going on concurrently since the Stresa meeting is the investigation of ASTM D670–42T (now under the designation D1313–54). It had been agreed to determine test values for all the "national" and Insulating Reference Oils by ASTM D670–42T, Method B, the bomb test for transformer oils. While only a limited number of members initially had the apparatus available F. Clark of the U.S.A. arranged for a bomb to be circulated among members. This did not become available in the U.K. until 1955 and, in the meantime, apparatus had been obtained by the British Electricity Authority; the results of their work, which were made available to IEC, have been published in part in a paper to the IP by Ward.[10]

Part of the work was carried out upon the Insulating Reference Oils, and the relative assessments of these were in general similar to those obtained by the IEC oxygen blowing method with copper wire catalyst at 100° C or 110° C. A minor difference showed itself in the favouring of I.R.O. 1, the solvent-refined distillate, in relation to I.R.O. 3 with regard to sludge formation.

Considering the results internationally, the reproducibility obtainable with the bomb test was initially found to be very poor. Although nominally the same oils had been used in each laboratory, the work had been spread over a rather long period of years, during which, it was felt, significant changes in the oils might have taken place. It was agreed in 1955 to circulate two new oils internationally for further tests under rigidly standardized conditions, *n*-heptane being used as sludge precipitant.

In the U.K. the laboratories of the Metropolitan-Vickers Electrical Co. Ltd and of the Central Electricity Authority took part. All the work contributed from various countries was found to be in good agreement. It appears that the test is potentially useful, as it has been shown also to have possibilities of application to inhibited oils by the introduction of soluble catalysts. The rather high cost of the apparatus has militated against its adoption as an international test, and no further work with the bomb method has been proposed by IEC, nor is planned immediately in the U.K.

INVESTIGATION OF FUNDAMENTAL MECHANISMS IN OIL OXIDATION

It has been felt for several years in ERA Section E that further progress in the improvement of oils with regard to oxidation in service, and in the development of laboratory testing methods for this property, would be very much assisted by a more fundamental knowledge of the mechanism of low temperature oxidation of mineral oils. It was accordingly proposed to sponsor work in this field to be carried out at universities.

As a first step Professor F. Morton, then of Birmingham University, was asked to prepare a detailed survey of the literature, and to make suggestions as to the most useful directions for further work. Part of the survey, in the form of a critical résumé, was made available to IEC in 1955, and is presented in a condensed form at this symposium [7]; the author is continuing to take an active part in the work of ERA in this field. In 1956 programmes were agreed for work at Liverpool and Birmingham Universities and papers respectively by Bawn and Moran [8] and by Robb and Shahin [9] are now offered as the first fruits of this policy. In addition, the group of industrial laboratories, working in close consultation with the above workers, have undertaken supplementary work, which is included in the paper by Thompson.[5]

FURTHER COLLABORATION WITH IEC

In the meantime, further work direct for IEC in this field has been discontinued, as it has been felt that the resolution of more fundamental problems could usefully have priority. Nevertheless, the identity of aims ensures a continuation of collaboration. The discussion at this symposium of the work reported in several papers will naturally be closely considered by ERA with this in view.

At a further plenary meeting of IEC Technical Committee No. 10 held in 1956 at Munich the discussion had mainly to do with the electric strength of transformer oil, work upon which has now been carried out by ERA on behalf of IEC, but which is not within the scope of the present paper. Nevertheless, it became evident that, following the publication of the Sub-Committee report,[2] several additional countries were investigating the proposed oxidation test techniques. It was reported that certain countries, notably those having existing standard tests of rather long duration or in which unduly high temperatures had been retained, were already tentatively using the method with one or other of the alternative catalytic conditions which had been suggested, in the meantime as a test in parallel with their existing standard method.

Professor Weiss, in discussing the present aims of the IEC work, has stated that the provision of a common language for describing transformer oils is the first step. This has clearly to a large measure been achieved so far as technique is concerned, and it remains to reach agreement upon catalytic conditions and test temperature before there can be taken the further step of submission to the International Standardization Organization.

ACKNOWLEDGMENTS

The author wishes to express his thanks to the various organizations mentioned above who have collaborated in experimental work for the ERA and for the permission of the latter to publish this paper.

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A THERMOCOUPLE METHOD OF STUDYING OXIDATION REACTIONS. PART I. PHOTOSENSITIZED OXIDATION OF *CYCLO*HEXENE *

By J. C. ROBB † and M. SHAHIN †

SUMMARY

A method is described for studying the non-stationary state of oxidation reactions by following the rise in temperature of the reacting mixture. The rate of oxidation and the corresponding lifetime have been obtained from the temperature–time curves.

The photochemical oxidation of *cyclo*hexene (at 40° C) has been studied as an example, and the rate constants for the propagation and termination reactions obtained are compared with the values recorded in the literature. The rate of initiation has been measured by using 2,6-di-*t*-butyl-*p*-cresol as a retarder, and the mechanism put forward by Burnett and Melville [6] has been confirmed.

INTRODUCTION

THE low temperature oxidation of hydrocarbons, and olefins in particular, has been subject to a great deal of investigation for many years. The chain mechanism nature of the reaction, which was originally postulated by Bolland and confirmed by many workers,[1, 2] has long been accepted, and data on oxidation of many hydrocarbons are now available. Yet the method generally used in these investigations (*i.e.* following the reaction rates by measurements of oxygen absorption) suffers from the following disadvantages:

(1) The oxygen take-up may be dependent on the speed of shaking the reaction mixture.

(2) Gas-phase reaction takes place simultaneously in the region just above the surface of the liquid.

(3) The rate of reaction is dependent on the pressure of oxygen above the liquid.

(1) and (3) are usually overcome by working at high speed of shaking and high oxygen pressure or using a thin film (*ca* 1 mm thickness) of the hydrocarbon, so that the diffusion of oxygen into the system does not become rate-determining. It is also possible to use the reaction mixture in the form of a froth in order to obtain high surface area where oxygen and hydrocarbon can interact.

Lack of precision and facility also exist in the sector method of intermittent illumination which has been used to measure the lifetime of the radicals.[3] Apart from the fact that a complete experiment takes several hours, the thermally initiated reaction which progressively increases in significance complicates the analysis of the results and intrinsically reduces the accuracy [4] of the method.

The method described below is a thermometric one, a modified version of that used by Bengough and Melville [5] in following the non-stationary state of polymerization. It is based on using a single thermocouple junction as a temperature sensitive element in conjunction with a low impedance d.c. amplifier and a suitable recording system depending on the lifetime of the radicals in the reaction. The thermocouple is situated in the centre of the reaction vessel and measures the temperature of this region only. Since the whole of the reaction vessel is heated uniformly through chemical reaction, and cooling only occurs at the walls of the vessel, the reaction at the centre will remain adiabatic for longer periods than at other regions of the vessel.

The reaction which is photochemically induced and automatically recorded is in this case between the hydrocarbon and the dissolved oxygen. The amount of oxygen available in this way is sufficient for 10–15 minutes of reaction before its concentration drops below the rate-determining value. While the reaction

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remains adiabatic, the rate at which the reacting mixture is heated is directly proportional to the fraction of the hydrocarbon which has been oxidized. From the established kinetics of autoxidation of hydrocarbons at high oxygen concentration we have:

Initiation: $\quad R^{\cdot} \qquad R_i$

Propagation: $\quad \begin{cases} R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} & K_2 \\ RO_2^{\cdot} + RH \longrightarrow RO_2H + R^{\cdot} & K_3 \end{cases}$

Termination: $\quad 2\,RO_2^{\cdot} \longrightarrow X \qquad K_6$

one derives the equations:

$$\frac{d(R^{\cdot})}{dt} = R_i - K_2\,(R^{\cdot})(O_2) + K_3\,(RO_2^{\cdot})(RH). \quad (1)$$

and

$$\frac{d(RO_2^{\cdot})}{dt} = K_2\,(R^{\cdot})(O_2) - K_3\,(RO_2^{\cdot})(RH) - K_6(RO_2^{\cdot})^2\,. \quad (2)$$

Equation (1) can be equated to zero, as the lifetime of R· radicals is very short in comparison with that of the $RO_2^{\cdot}$ radicals. An estimate of the lifetime of $R^{\cdot}$ radicals can be obtained in the case of ethyl linoleate, as values for K_2 and the absorption coefficient of oxygen are available.[4]

$$\tau = \frac{1}{K_2(O_2)} = 2 \times 10^{-5}\ \text{sec}$$

Therefore:

$$(R_i) = K_2\,(R^{\cdot})(O_2) - K_3\,(RO_2^{\cdot})(RH)$$

or

$$\frac{d(RO_2^{\cdot})}{dt} + K_6\,(RO_2^{\cdot})^2 - R_i = 0$$

which on integration gives: *

$$(RO_2^{\cdot}) = (RO_2^{\cdot})_s \tanh t/\tau$$

where $(RO_2^{\cdot})_s$ = concentration of peroxy radicals at stationary state and τ = lifetime of the radical chain.

It follows therefore that the rate of reaction =

$$\frac{-d(RH)}{dt} = K_3(RH)(RO_2^{\cdot}) = K_3(RH)(RO_2^{\cdot})_s \tanh t/\tau$$

from which:

$$F = \frac{K_3}{K_6} \ln \cosh t/\tau \quad . \quad . \quad . \quad (3)$$

where $F = \dfrac{(RH)_0 - (RH)}{(RH)_0}$ and $(RH)_0$ = initial hydrocarbon concentration.

When t exceeds 3 τ equation (3) approximates to a straight line

$$F = \frac{K_3}{K_6}\,(t/\tau - \ln 2)$$

$$\text{intercept} = (\ln 2).\tau \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which intersects the time axis at τ ln 2, and whose slope is equal to $\dfrac{K_3}{K_6}\dfrac{1}{\tau}$. Thus a knowledge of the heat of reaction will enable one to measure $\dfrac{K_3}{K_6}$ and τ readily from the plot of temperature rise against time. It is also apparent that since the reaction occurring in the centre of the reaction vessel proceeds adiabatically (for approximately 30 sec), the rate of reaction will be directly proportional to the rate of rise of temperature.

The time required for each determination is about 30–40 sec, and thus it is possible to make a number of measurements on a single sample. When the supply of oxygen is exhausted the hydrocarbon can be resaturated with oxygen and used again.

EXPERIMENTAL

Apparatus

The reaction vessel shown in Fig 1 is basically similar to the dilatometer which Bengough and

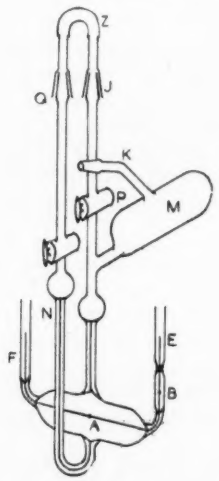


FIG 1

DIAGRAM OF THE REACTION VESSEL

Melville [5] used. It has a capacity of *ca* 15 ml and is made of hard glass with a Pt/Pt–Rh (13 per cent) thermocouple *A* sealed into the bulb and a balancing thermocouple *B* sealed in a glass tube just outside the vessel. A few ml of mercury in each of the glass

* Details of this derivation have been given by Burnett, G. M. *Trans. Faraday Soc.*, 1950, **46**, 772.

tubes E and F make electrical contact between the ends of the thermocouple wires and the screened leads which are connected to the input terminals of a Tinsley d.c. amplifier,* Type 5132. The leads are covered by sheaths of rubber tubing which are slipped

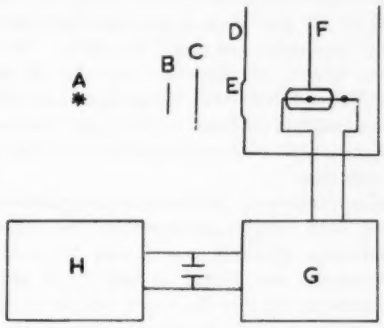


FIG 2

DIAGRAM OF THE APPARATUS

A—mercury arc
B—OX1 filter
C—shutter
D—thermostat bath
E—window
F—reaction vessel
G—amplifier
H—recorder

over the side tubes (E and F) of the reaction vessel. The capillary N is used to bubble oxygen through the hydrocarbon. A diagram of the arrangement of the different parts of the apparatus is shown in Fig 2.

The thermocouples are made from 0·10-mm dia platinum and platinum–rhodium (13 per cent) wires welded together in a small electric arc from a 6-volt battery.

The water bath is a glass tank lagged with 3-inch thick glass fibre on all sides (except for a small window through which the reaction vessel is irradiated) and is equipped with the usual mercury–toluene regulator.

A Tinsley recording voltmeter with a resistance of 350 Ω and a range of 0–5 mA is used to record the output of the amplifier. A 25-μF paper condenser is mounted across the output to smooth out the basic noise of the amplifier.

The light source for the photochemical reaction is a 125-W Osira mercury arc, stabilized with a constant voltage transformer. Radiation of wavelength less than 3000 Å and greater than 4000 Å is eliminated by a Chance 0X1 filter placed between the source and the bath containing the reaction vessel.

The shutter consists of a sheet of aluminium (4 inches × 4 inches) hung from a piece of fuse wire, and in series with a variable resistance (total 5 Ω), a switch, and a 1·5-volt low tension radio battery. On cutting the fuse wire the shutter opens, and simultaneously a signal is induced in the input circuit. This appears as a pip on the final recorder trace, thus marking accurately the time when irradiation starts.

Procedure

The reaction vessel is connected to the high vacuum line at the joint J with the bulb M vertical. The required amount of the photosensitizer, dissolved in A.R. benzene, is introduced into this bulb through the side-arm K, and the solvent is pumped off. A known volume of hydrocarbon contained in a reservoir attached to the line is distilled under vacuum into this bulb by cooling it in liquid air. The tap P is then closed and the vessel is taken off the line. The mixture in the bulb M is warmed up and tipped into the cell while still under vacuum. Pure oxygen, after passing through a liquid air trap, is then bubbled through the solution via capillary N. Throughout this operation the reaction vessel is kept in a cold bath (*e.g.* methanol + CO_2) to minimize the evaporation of hydrocarbon. After saturation (20–30 minutes) the two limbs J and Q are joined by the bent tube Z. The screened leads are dipped into the mercury of the two side-tubes and sleeved by rubber tubing to protect them from contact with the water of the thermostat. The reaction vessel is then placed in the thermostat and held in a fixed position by means of a rigid stand. The cover is placed on the thermostat and the system left for 15 minutes to attain thermal equilibrium. Normal thermostatic controls maintain a constant temperature to within $10^{-2°}$ C, while for the short time (1 minute) during which the experiment is carried out, variation in temperature should be less than $5 \times 10^{-4°}$ C (at 30° C). To achieve this, the controls are switched off and the water of the thermostat allowed to settle for 20–40 minutes (depending on the working temperature), thus eliminating the movement of hot and cold streams. A temperature gradient is thus set up. This keeps the central zone of the thermostat, where the reaction vessel is situated, within the required temperature limits. Both the amplifier and the mercury arc are switched on for about ½ hour before the experiment so that they give steady outputs. The sensitivity of the amplifier is then adjusted and

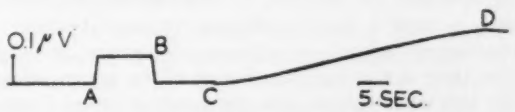


FIG 3

A TYPICAL CALIBRATION AND REACTION TRACE

The points A and B indicate the times at which the test voltage is applied and removed. C shows the opening of the shutter, and D when the shutter is replaced.

* The details of the amplifier are given in Bengough's paper.[5]

a test signal voltage is switched on for about 5 seconds and then switched off (for calibration purposes). The mercury arc shutter is subsequently opened and kept open until the rate of rise of temperature recorded by the pen is constant (*ca* 30 sec). A recorder trace of a typical experiment is shown in Fig 3.

Limitations of the Method

The errors involved in the method and the ultimate sensitivity of the instrument are described.[6] However, the delay in the recording of the full signal was only about 0·5 sec compared with a few seconds in the arrangement used by Bengough.

PHOTOSENSITIZED OXIDATION OF *CYCLO*HEXENE

Materials

(1) *cyclo*Hexene. A commercial sample was fractionally distilled over copper stearate, and subjected to two more distillations under vacuum.

(2) 1-Azo-*bis*-1-*cyclo*hexane carbonitrile. A commercial sample was recrystallized from aqueous alcohol. M.p. = 114°–114·5° C. This compound has an absorption peak in the region of 3500 Å with a molar extinction coefficient of 16.

(3) 2,6-di-*t*-butyl-*p*-cresol. Sublimed under vacuum. M.p. = 68·5°–69·5° C.

(4) *N*-phenyl-β-naphthylamine. Recrystallized from petroleum ether (80°–100°). M.p. = 108·5°–109·5° C.

(5) Benzene. AnalaR grade.

Experimental Results

Preliminary experiments carried out on the following systems: (*a*) benzene, (*b*) benzene + photosensitizer + oxygen, (*c*) *cyclo*Hexene, (*d*) *cyclo*Hexene + photosensitizer, (*e*) *cyclo*Hexene + oxygen, showed that there is a general heating-up of the system when the shutter is opened and the reaction vessel irradiated. There was little difference in its value from system to system. Table I shows the values of this heat for *cyclo*hexene and initiator. The values of this heat at reduced light intensities were measured by inserting screens of known transmissions between the light source and the thermostat. Successive experiments were carried out on a single sample. The sample size for all the experiments which were carried out on *cyclo*hexene was 15 ml and the initiator concentration $0{\cdot}785 \times 10^{-2}$ mol/litre.

TABLE I

Stray Radiation

100% transmission	52% transmission	33% transmission
$2{\cdot}20 \times 10^{-3}$ μV/sec	$1{\cdot}22 \times 10^{-3}$ μV/sec	$0{\cdot}86 \times 10^{-3}$ μV/sec
2·40	1·29	0·75
2·27	1·31	0·67
2·35	1·20	0·71
2·23	1·18	0·66

The magnitude of this heating was found to be temperature-independent (investigated at 30°, 40°, 50°, and 60° C), and showed no induction period. Its intensity exponent was equal to unity. Its magnitude was found to diminish only by 30 per cent when a Chance ON20 filter (absorbing infra-red radiation) was inserted in front of the light source. This heat is the result of direct irradiation of the thermocouple junction.

Using a mixture of *cyclo*hexene and photosensitizer saturated with oxygen, an increased heating-up with an observable lifetime was found to occur. The oxygen supply was found to last for a number of determinations (Table II), and, on saturating the sample for the second and the third time, the rate of production of heat remained unchanged.

To obtain the heat due to the reaction, heat due to stray radiation (Table I) is to be deducted from the total heat (Table II). An examination of Tables I and II indicates that the heat due to stray radiation is about 50 per cent of the total heat. However, the heat due to stray radiation was reduced in later experiments to only 15 per cent of the total by broadening the beam of light so that some radiation fell on the reference junction.

TABLE II

Rate of Production of Heat

100% transmission, first saturation	100% transmission, second saturation	100% transmission, third saturation
$4{\cdot}20 \times 10^{-3}$ μV/sec	$4{\cdot}39 \times 10^{-3}$ μV/sec	$4{\cdot}34 \times 10^{-3}$ μV/sec
4·17	4·32	4·44
4·37	—	—
4·46	—	—
4·20	—	—

To confirm the relationship between the rate of reaction and the rate of initiation, the heat produced at reduced intensities (51 per cent, 46 per cent, and 31 per cent transmission screens) was then measured and the results plotted against (intensity)$^{\frac{1}{2}}$. This is shown in Fig 4. The dependence of lifetime on the intensity of illumination was also found by plotting $\log_{10}$ (lifetime) against $\log_{10}$ (intensity) as shown in Fig 5.

As:

$$\tau = \frac{\text{concentration of active radicals}}{\text{rate of removal of radicals}}$$

$$= \frac{(RO_2^{\cdot})}{K_6(RO_2^{\cdot})^2} = \frac{1}{K_6\,(RO_2^{\cdot})}$$

It follows, from the kinetics of the steady state that:

$$R_i = K_6 (RO_2^{\cdot})^2$$

and therefore:

$$\tau = \frac{1}{K_6^{\frac{1}{2}} R_i^{\frac{1}{2}}} \cdot \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The line in Fig 5 has the slope of $-\frac{1}{2}$ as expected from equation (5).

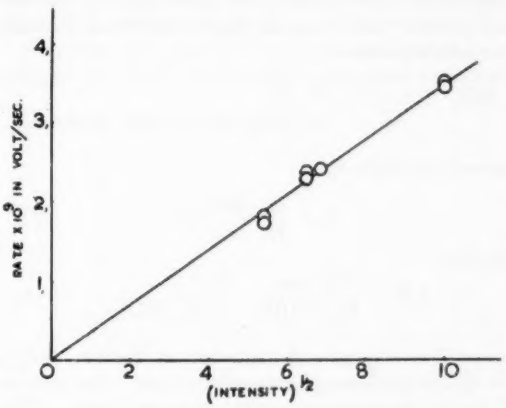


FIG 4

VARIATION OF THE RATE WITH LIGHT INTENSITY: OXIDATION OF *cyclo*HEXENE AT 40° C

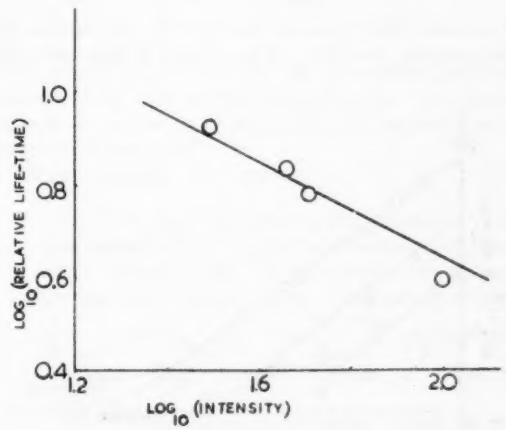


FIG 5

VARIATION OF THE LIFETIME WITH LIGHT INTENSITY: OXIDATION OF *cyclo*HEXENE AT 40° C

As the rate of reaction at the steady state[3] is given by

$$\text{Rate} = \frac{K_3}{K_6^{\frac{1}{2}}} (RH) (R_i)^{\frac{1}{2}}$$

it follows that:

$$\tau = \frac{K_3 (RH)}{K_6 (\text{rate})} \cdot \quad . \quad . \quad . \quad . \quad (6)$$

and thus equations (4) and (6) give

$$\text{Intercept} = C + \frac{K_3 (RH)}{K_6 (\text{rate})} \ln 2$$

where C is the lag in response of the apparatus in seconds. Hence a plot of measured intercept against

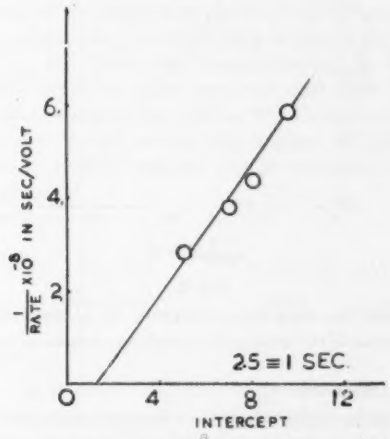


FIG 6

VARIATION OF THE RATE WITH LIFETIME: OXIDATION OF *cyclo*HEXENE AT 40° C

the reciprocal of rate is a straight line which cuts the measured intercept axis at a time equal to C, and whose slope is equal to $\frac{K_3(RH)}{K_6} \ln 2$. Fig 6 shows that the lag on this instrument is 0·5 sec. Once the lag of the recorder has been ascertained it is possible to obtain the value of the lifetime from a single measurement.

Energy of Activation

The rate of reaction and the lifetime of the radicals were measured at three different temperatures (30°, 40°, and 50° C). The overall energy of activation ($E_3 - \frac{1}{2}E_6$) of the reaction was found from the plot

TABLE III

Lifetime (in sec)

$\tau \ln 2$, 30° C	$\tau \ln 2$, 40° C	$\tau \ln 2$, 50° C
1·7	1·5	1·7
1·5	1·7	1·7
1·5	1·5	1·5
1·5	—	—

The above values are the measured intercept minus the recorder lag.

of $\log_{10}$ rate against $1/T$ to be equal to 7·0 k.cal/mol (Fig 7). The values of the lifetime at these temperatures are shown in Table III.

The variation observed in Table III is within the

limits of the experimental error and is independent of temperature. Thus from equation (5) it is clear that $E_6 = 0$ and hence $E_3 = 7{\cdot}0$ k.cal.

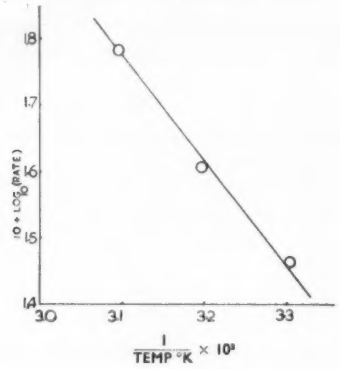
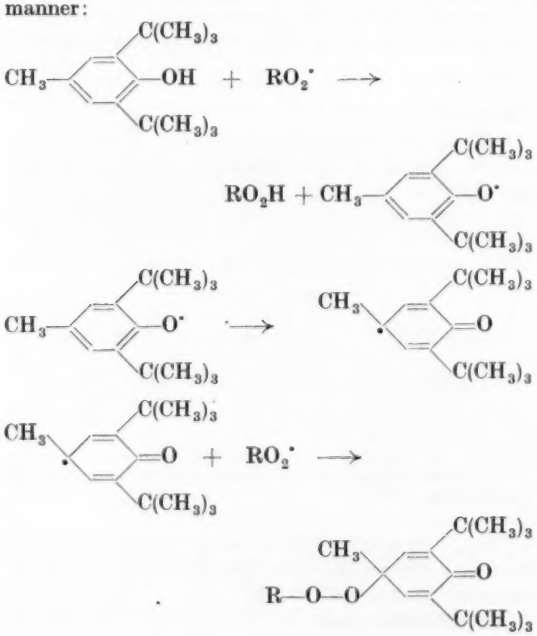


FIG 7

ARRHENIUS PLOT FOR OXIDATION OF *cyclo*HEXENE
Each point is the average of a number of measurements.

Rate of Initiation

To evaluate the absolute velocity constant of the propagation and termination step, the rate of initiation has to be known. This is commonly measured by the use of inhibitors. The choice of an inhibitor is arbitrary and differs from system to system. In this case 2,6-di-*t*-butyl-*p*-cresol was used because it is a well-known anti-oxidant and its mode of action with the peroxy radicals is relatively simple. It is known [6,7] that every molecule of the above phenol will terminate two chain carriers in the following manner:



The product of inhibition is colourless and inactive to further reaction.

The rate of oxidation at the temperatures investigated was low (*ca* 10^{-6} mol/litre/sec) and the supply of oxygen available for reaction limited, therefore a low concentration (*ca* 10^{-4} mol/litre) of the inhibitor was chosen and the retardation effect studied by measuring the rate of reaction after intervals of irradiation.

The kinetics of interaction of an inhibitor molecule with chain carriers has been dealt with by Burnett and Melville [8] and it can be shown that when termination solely occurs by:

$$RO_2^{\cdot} + \text{In} \longrightarrow X \quad K_7$$

In being the inhibitor molecule,

the rate of oxidation

$$R = \frac{K_3\,(RH)}{K_7\,(\text{In})}\,R_i \quad . \quad . \quad . \quad (7)$$

and also

$$1/R = \frac{K_7\,(\text{In})_0}{K_3\,(RH)R_i} - \frac{K_7}{n\,K_3\,(RH)}\,t \quad . \quad (8)$$

where R is the rate of oxidation at time t; $(\text{In})_0$ is the initial inhibitor concentration, and n the number of chains stopped by one inhibitor molecule. Thus a plot of $^1/R$ against t will give a straight line and hence:

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{R_i}{n\,(\text{In})_0}$$

It is also clear that at time $t = 0$, $^1/R$ is directly proportional to $(\text{In})_0$. Figs 8 and 9 illustrate the

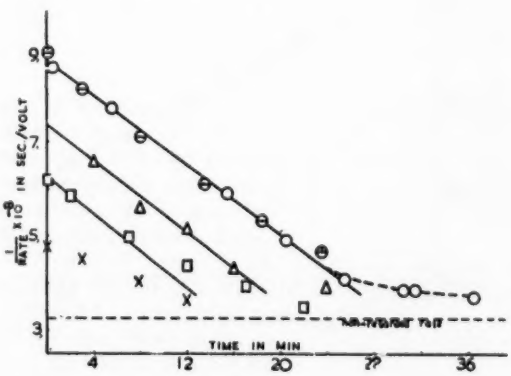


FIG 8

PHOTOSENSITIZED OXIDATION OF *cyclo*HEXENE (40° C) RETARDED BY 2,6-DI-*t*-BUTYL-*p*-CRESOL

Inhibitor concentration $(\text{In})_0$ for O and ⊖ is $1{\cdot}42 \times 10^{-4}$ mol/litre, for Δ is $1{\cdot}18 \times 10^{-4}$ mol/litre, for □ is $0{\cdot}94 \times 10^{-4}$ mol/litre, and for X is $0{\cdot}71 \times 10^{-4}$ mol/litre.

above relationship and show that equation (8) only holds when the $(\text{In})_0$ is high enough for mutual termination of peroxy-radicals to be completely

suppressed. The rate of initiation R_i found in this way was $1{\cdot}0 \times 10^{-7}$ mol/litre/sec.

The retarded rates at reduced light intensities were also measured. The values found for the intensity exponent were 0·8–0·9. These measurements were possible only when the sample had already been irradiated for a considerable time so as to give measurable rates at reduced intensities. Thus they might represent the period when the change in the mechanism of reaction from "retarded" to "non-retarded" has been taking place.

Equation (8) (when $t = 0$) enables one also to calculate K_7, since all the other parameters are known.

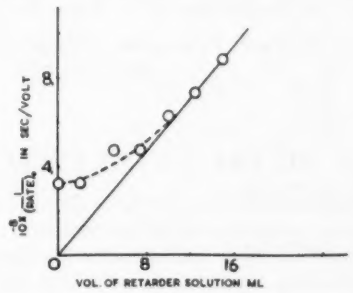


FIG 9

VARIATION OF THE INITIAL RATE WITH RETARDER CONCENTRATION

Every ml of retarder solution corresponds to a retarder concentration of $0{\cdot}94 \times 10^{-5}$ mol/litre.

The values of K_7 at 30° C and 40° C are 6080 litre/mol/sec and 7620 litre/mol/sec respectively. This corresponds to an energy of activation for the retardation step of 4·5 k.cal/mol.

Other inhibitors used were:

(i) *N*,*N*′ diphenyl-*p*-phenylene diamine. This was found to be a very strong inhibitor (5–6 times more efficient than 2,6-di-*t*-butyl-*p*-cresol) and formed an intense yellow product (probably during the reaction. This product is also an effective inhibitor.[7]

(ii) *N*-phenyl-2-naphthylamine. This is 2–3 times stronger than 2,6-di-*t*-butyl-*p*-cresol, and gives a pale yellow product which is also an inhibitor.

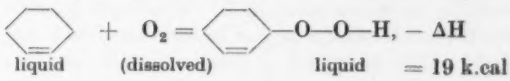
(iii) Di-phenyl-picryl hydrazyl (DPPH). This compound was found to be decolorized by an oxidized sample of *cyclo*hexene. This suggests that DPPH takes part in other reactions as well as retardation, and therefore a simple kinetic scheme does not apply in this case.

(iv) Benzoquinone. This was found to be a very weak inhibitor.

Heat of Reaction

The value of velocity constant for the propagation step (K_3) found by this method is dependent on the heat of the overall reaction ($RH + O_2 \longrightarrow RO_2H$). To establish the validity of this method for studying the oxidation reactions, it was thought convenient to obtain the heat of the above reaction by determining the heat of combustion of *cyclo*hexene hydroperoxide. Pure *cyclo*hexene hydroperoxide is extremely difficult to prepare. However, determination on the two samples available (85·6 per cent and 90·6 per cent pure) gave values very close to 872·9 k.cal/mol. This, together with the heat of combustion of *cyclo*hexene (891·9. k.cal/mol) enables one to calculate the heat of reaction.

Therefore:



Calculations

The numerical relationship between the rate of oxidation and the rate of rise in temperature can be obtained by using the following information:

molecular weight = 82
specific heat (40°C) = 0·448
heat of reaction = 19 k.cal/mol

and the emf temperature relationship for Pt/Pt–Rh thermocouples at 40° C.

$$1^\circ\,C \equiv \frac{1000}{158}\,\mu V$$

thus:

a rate of 1 per cent per hour $\equiv 0{\cdot}952 \times 10^{-2}\,\mu V$/sec

and a rise in temperature corresponding to $3{\cdot}09 \times 10^{-3}$ μV/sec for the oxidation of *cyclo*hexene at 40°C would be equivalent to $9{\cdot}2 \times 10^{-6}$ mol/litre/sec.

Conclusion

The thermocouple method of following the oxidation of hydrocarbons is unique in that it provides a convenient method of studying the early stages of the reaction and enables the lifetime of the reacting

TABLE IV

Collected Results

	This work (40° C)	Previous work (40° C)
Rate of oxidation	$9{\cdot}2 \times 10^{-6}$ mol/litre/sec	—
Rate of initiation	$1{\cdot}01 \times 10^{-7}$ mol/litre/sec	—
Lifetime of the radical chain	2·5 sec	—
Chain length	90	30 [9]
K_3	3·7 litre/mol/sec	1·97 litre/mol/sec [9]
$E_{overall}$	7·0 k.cal/mol	8·1 k.cal/mol [9]
K_6	$1{\cdot}6 \times 10^9$ litre/mol/sec	$0{\cdot}95 \times 10^9$ litre/mol/sec [9]
E_6	0	<5 k.cal [9]
E_3	7·0 k.cal/mol	8·5 k.cal/mol [9]
E_7 2,6-di-*t*-butyl-*p*-cresol	4·5 k.cal/mol	—
K_7 2,6-di-*t*-butyl-*p*-cresol	7620 litre/mol/sec	—

species to be readily obtained. It also allows the rate measurement to be carried out within a very short period of time. Thus, these measurements are unaffected by either the dark reaction or any side-reaction due to the products of oxidation.

The method is also applicable to the study of the behaviour and efficiency of the retarders which need be present only in small concentrations.

The results are collected together in Table IV. The quantitative information obtained here is in general agreement with such previous values as are available.

ACKNOWLEDGMENTS

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KINETICS OF LOW TEMPERATURE METAL-CATALYSED HYDROCARBON OXIDATION *

By C. E. H. BAWN † and D. P. MORAN †

SUMMARY

The nature and the mechanism of the catalytic action of trace metals in autoxidation reactions is discussed. It is shown that in general the oxidation proceeds by a chain reaction initiated by an electron transfer reaction of the higher valence state of the metal ion with the reactant or with the thermally-formed hydroperoxide. Some preliminary results on the copper-stearate-catalysed oxidation of ethylbenzene at 80° C are presented. It is concluded that the reaction occurs by the well-established radical chain mechanism leading to peroxide formation, and that the metal salt catalyst complexes with the hydroperoxide formed. The work was carried out at the University of Liverpool.

INTRODUCTION

It is now generally accepted that the oxidation of hydrocarbons by air or molecular oxygen is a chain reaction. The rate of the oxidation may be accelerated by ultra-violet light, added peroxides, peroxidic products of the oxidation or other free radical producing substances, and by certain salts of the heavy metals. In general, the primary product of the liquid phase oxidation of both saturated and unsaturated hydrocarbons (RH) is a hydroperoxide (ROOH) and much investigation substantiates the view that the formation of this hydroperoxide arises from a chain reaction of the following type:

$$RH \longrightarrow R\cdot \quad \text{Initiation} \quad (1)$$

$$\left.\begin{aligned} R\cdot + O_2 &\longrightarrow RO_2\cdot \quad (2)\\ RO_2\cdot + RH &\longrightarrow ROOH + R\cdot \quad (3)\end{aligned}\right\} \text{Propagation}$$

$$\left.\begin{aligned} R\cdot + R\cdot &\quad \ldots \quad (4)\\ R\cdot + RO_2\cdot &\quad \ldots \quad (5)\\ RO_2\cdot + RO_2\cdot &\quad \ldots \quad (6)\end{aligned}\right\} \longrightarrow \text{products} \quad \text{Termination}$$

The results of numerous kinetic studies are in agreement in showing that the initiating reaction, which will be discussed in more detail later, is the formation of a free radical R·, RO·, or RO_2·, where RH is the hydrocarbon. Many variants of this scheme have been observed and these are determined by the nature of the initiating system, and the structure of both the hydrocarbon and the intermediate products.

INFLUENCE OF STRUCTURE ON RATE OF OXIDATION

The ease of oxidation of a hydrocarbon in the liquid state or in solution is very dependent on its molecular structure and certain broad generalizations have been reached from kinetic studies.

(1*a*) In the normal paraffin series CH_3–$(CH_2)_n$–CH_3 the point of initial reaction is more or less random among the methylene groups and there seems to be no specificity of attack.

(1*b*) In comparison with normal paraffins the

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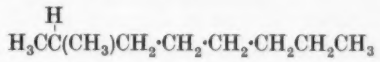
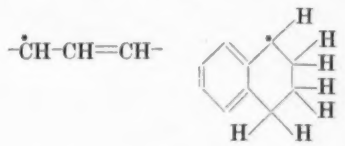
† Department of Inorganic and Physical Chemistry, University of Liverpool.

branched hydrocarbons are usually oxidized much more easily and in general a tertiary C–H bond as in, for example, 2-methylheptane



is the preferred site of reactions.

(2) Unsaturated hydrocarbons are very readily oxidized at relatively low temperatures and in many cases the hydroperoxide formed can be isolated in very high yields. From studies of the structure of the hydroperoxide formed, Farmer and others showed that the initial oxygen or free radical reaction occurred at the methylene group adjacent to the double bond, namely,



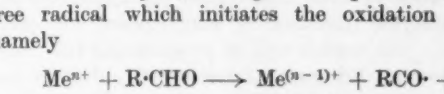
(3) As with the other hydrocarbons, the point of attack in aromatic and hydro-aromatic molecules by either oxygen or a free radical is at the weakest C–H bond. The oxidation of side chain aromatic hydrocarbons occurs preferentially at the side chain –CH rather than in the ring. Thus, although naphthalene is itself relatively stable to oxidation, part hydrogenation of the molecule leads to very enhanced rates of oxidation. This is in line with the conclusions under (2).

The above general relations will not necessarily apply to mixtures of hydrocarbons. The least stable component in a mixture is not necessarily oxidized in preference to the more stable one. The oxidizability is determined by interaction phenomena between the various molecules and radicals, as may be readily seen by writing down the propagation and termination reactions in accordance with the free radical mechanism discussed above.

METAL-CATALYSED OXIDATION

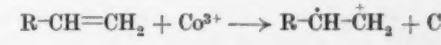
Small amounts of the salts of the heavy metals catalyse a wide variety of autoxidation reactions, *e.g.* saturated and unsaturated hydrocarbons, aldehydes, degradation of rubbers and high polymers, and the drying of oils. Although many of these reactions are of great technological importance, the occurrence of metal-catalysed oxidation in processing, handling, and storage of materials often leads to the development of unwanted and undesirable properties. For example, the oxidation of transformer oils and the consequent objectionable development of acidity and formation of sludge.

An understanding of the influence of metals and soluble and insoluble metal salts on the kinetics and course of the oxidation reactions of simple hydrocarbons will have a direct bearing on, and help one to understand, the reactions occurring in complex hydrocarbon mixtures. Extensive experimental studies with soluble metal salt catalysts have shown that there is a marked specificity in their action, cobalt and manganese salts being in general most effective. Results obtained using soluble metal soaps indicate that the organic part of the salt has no pronounced effect on the oxidation rate.[1] Much valuable information on the nature and function of the catalyst has been obtained from measurement of the oxidation of aldehydes.[2] In these systems the onset of oxidation corresponded with a change in valency state of the metal. Thus, with a soluble cobaltous salt, commencement of oxygen uptake coincided with a change from the pink to the green colour of the trivalent state. With manganous salts the onset of oxidation corresponded to the formation of the manganic ion. Similar transformations have been observed in the oxidation of both saturated and unsaturated hydrocarbons, even when initially insoluble catalysts were employed. In the latter cases the slow autocatalysis of the oxidation was accompanied by solution of the catalyst due to the formation of a hydroperoxide, which functions as a weak acid and is itself the precursor of the normal acid products of the oxidation. Experiments on the oxidation of acetaldehyde and benzaldehyde in glacial acetic acid [2] have shown that the initiation reaction for cobalt, manganese, and copper salts is a direct electron transfer reaction of the higher valence state of the metal ion with the aldehyde, leading to the production of a free radical which initiates the oxidation chain, namely



where Me^{n+} is the metallic ion.

Similar measurements with unsaturated hydrocarbons have shown that whereas cobaltic ion in mineral acid solution interacted directly with the double bond by electron transfer with the formation of a reactive ion:



this reaction did not occur in glacial acetic acid or in the absence of free mineral acid.[3] This drastic change in catalytic effect has been shown to arise from the formation of stable cobaltic complexes. On the other hand, cobaltic salts readily react with hydroperoxide in the absence or presence of mineral or organic acid, and it has been shown that in the autoxi-

dation of olefins the metal salt-induced oxidation is initiated by a direct reaction between the metal ion or a metal complex and the hydroperoxide.[3] The latter is invariably present in minute amounts in hydrocarbons or is readily formed by a thermal reaction

$$Me^{n+} + ROOH \longrightarrow Me^{(n-1)+} + RO_2\cdot + H^+$$

Robertson and Waters,[4] and Wibaut and Strang [1] have postulated a similar initiation reaction in their studies on the autoxidation of tetralin and saturated hydrocarbons respectively. Other workers believe that soluble metal salt catalysts function by activating the oxygen.[5]

Very recently Chalk and Smith [6] have shown that the autoxidation of *cyclo*hexene catalysed by trace metals in non-polar media conforms to the broad scheme of the olefins and conclude that the initiation reaction is in general the breakdown of a catalyst hydroperoxide complex into free radicals, although catalyst–olefin or catalyst–oxygen interaction may be operative in the reactions of Co^{2+} and Cu^{2+} and 60° C. Dean and Skirrow, in this laboratory, have also obtained some evidence that cobaltous salt complexes with *tertiary* butyl hydroperoxide.

(1) *Copper Salt-Catalysed Oxidation of Ethylbenzene*

As part of the programme of investigation on insulating oils sponsored by the Electrical Research Association, we are studying the metal- and metal salt-catalysed autoxidation of some simple hydrocarbons. Copper and iron are the most common metallic contaminants of transformer oil, and in our initial work we have investigated the soluble copper-salt catalysed oxidation of ethylbenzene and *cyclo*hexene. The work is still in progress and this paper must be regarded as an interim report. The method and experimental procedure were as described by Bawn and Williamson.[7]

The oxidation of ethylbenzene was followed by direct measurement of the oxygen absorbed at 80° C and with copper stearate concentrations from 1×10^{-5} M (1·3 p.p.m.) to 5×10^{-2} M (6500 p.p.m.). The form of the oxygen uptake curve depended on the catalyst concentration, and two distinct types occur: (*a*) with catalyst concentrations of 1 to 10×10^{-5} M the volume of oxygen absorbed against time showed an initial acceleration period, followed by a long linear period and a gradual falling off in rate. The accelerating period was relatively short and corresponded to 0·2 to 0·5 per cent oxidation of the hydrocarbon. (*b*) With higher catalyst concentration ($1{\cdot}1 \times 10^{-4} - 5 \times 10^{-2}$ M) the absorption against time showed a relatively fast and approximately linear region which extended over 0·2 to 4 per cent of the oxidation according to the catalyst concentration. This was followed by a slower linear rate over the main course of the oxidation. The features of these well demarcated regions of catalysed oxidation are shown by the typical rate curves in Figs 1 and 2.

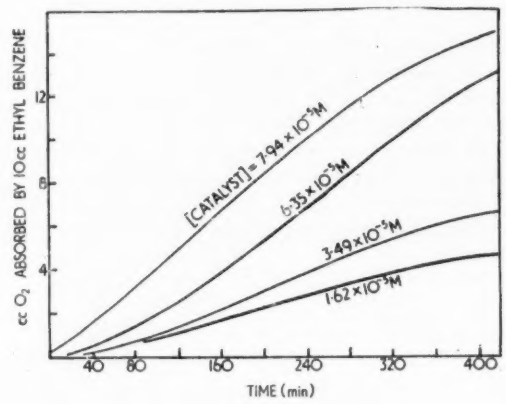


FIG 1

RATE OF OXYGEN ABSORPTION WITH TIME AND ITS VARIATION WITH CATALYST CONCENTRATION (EXPRESSED AS COPPER STEARATE) IN THE RANGE UP TO $1{\cdot}0 \times 10^{-4}$ M

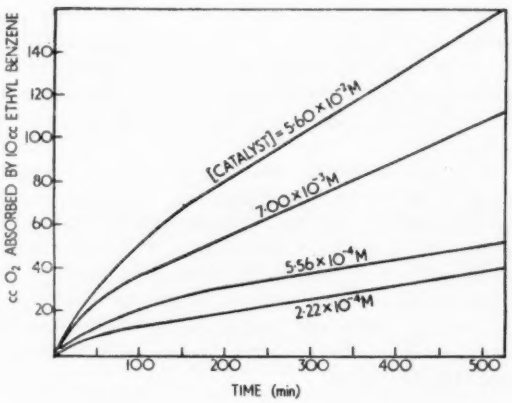


FIG 2

RATE OF OXYGEN ABSORPTION WITH TIME AND ITS VARIATION WITH CATALYST CONCENTRATION (EXPRESSED AS COPPER STEARATE) IN THE RANGE $1{\cdot}0 \times 10^{-4}$ TO 5×10^{-2} M

In each case the rate of oxidation was taken as the slope of the linear part of the curve following the initial rapid or autocatalytic period of the oxidation.

(2) *Dependence on Catalyst and Hydrocarbon Concentration*

A series of experiments was performed with the pure hydrocarbon (10 ml) and catalyst concentration in the two regions referred to above. These will subsequently be designated as low and high catalyst reactions, although it must be realized that the transi-

tion from one to the other is a continuous change. The variation of hydrocarbon concentration was studied by using purified diphenyl as an inert diluent at constant catalyst concentration. For each catalyst region the rate was directly proportional to the hydrocarbon concentration. Rate measurement for the initial reaction at high catalyst concentration showed a dependence on the square of hydrocarbon concentration. These results, showing the dependencies on catalyst concentration, are given in Figs 3 and 4, and are summarized by the following rate

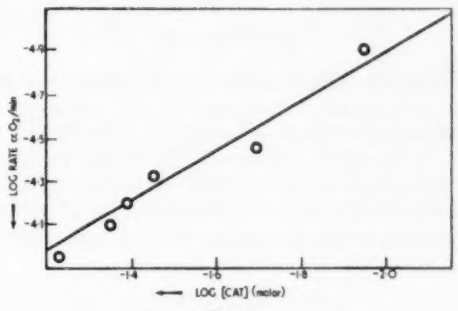


FIG 3

DEPENDENCE OF RATE ON COPPER STEARATE CONCENTRATION [$< 1 \times 10^{-4}$ M]

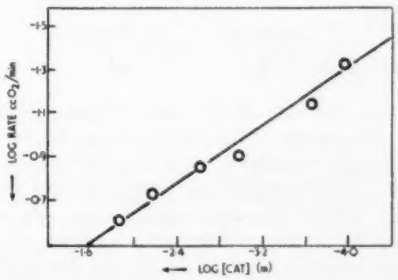


FIG 4

DEPENDENCE OF RATE ON COPPER STEARATE CONCENTRATION [$1 \cdot 0 \times 10^{-4}$ TO 5×10^{-2} M]

equations:

Low catalyst concentration

$$(1 - 10 \times 10^{-5}\ \text{M}) - [-d\text{O}_2/dt = 0 \cdot 26\ [\text{Cat}][\text{RH}]$$

High catalyst concentration

$$(1 \cdot 1 \times 10^{-4} - 5 \times 10^{-2}\ \text{M}) -$$

Initial linear rate:

$$-d\text{O}_2/dt = 2 \cdot 1 \times 10^{-4}[\text{Cat}]^{0 \cdot 34}[\text{RH}]^2$$

Main linear rate:

$$-d\text{O}_2/dt \propto [\text{Cat}]^{0 \cdot 34}[\text{RH}][\text{ROOH}]$$

In all cases the rate was independent of the oxygen pressure over the region 150 to 760 mm Hg.

PEROXIDE FORMATION

The formation of peroxide during the course of oxidation was followed by estimation of the peroxide by the method of Barnard and Hargrave.[8] For catalyst concentrations less than $1 \cdot 0 \times 10^{-4}$ M the peroxide formed was equivalent to the oxygen absorbed over the first 300 minutes of the oxidation (0·60 per cent hydrocarbon oxidized). The reaction was not followed beyond this period owing to its slowness. Initial additions of small amounts of hydroperoxide eliminated the accelerating stage (induction period) of the reaction (Fig 1) at low catalyst concentrations and the linear rate commenced at the origin. At higher catalyst concentration the peroxide yield was below that corresponding to the molal oxygen absorbed, except in the very early stages of the oxidation, and the increasing divergence between the oxygen absorption and peroxide curves became more noticeable the higher the catalyst concentration. Some typical results are recorded in the following tables. The difference between molal oxygen absorbed and the estimated peroxide curves is a measure of the extent of catalysed decomposition of the peroxide, and by plotting this difference against time

TABLE I

Relation of Oxygen Absorbed to Hydroperoxide Formed

Time (min)	Oxygen absorbed g mol/l $\times 10^{-3}$	ROOH g mol/l $\times 10^{-3}$
[Catalyst] = $1 \cdot 53 \times 10^{-4}$ M		
3	1·98	1·87
8	4·97	4·70
13	8·94	9·10
22	12·80	13·10
33	17·90	18·20
49	24·40	24·35
70	31·70	25·50
83	36·40	27·80
106	44·20	32·25
125	51·10	36·75
[Catalyst] = $5 \cdot 65 \times 10^{-4}$ M		
2	5·20	4·50
5	8·30	7·90
13	14·30	13·90
25	23·20	23·60
36	29·70	27·00
52	39·30	34·40
85	51·40	40·30
111	63·00	53·00
140	76·20	61·30
[Catalyst] = $10 \cdot 54 \times 10^{-4}$ M		
2	7·06	7·30
6	13·40	15·80
9	18·00	17·10
14	22·90	22·20
22	31·20	25·10
34	41·50	32·40
49	56·60	38·60
74	77·90	53·30
131	125·00	76·00

at various extents of reaction the rate of peroxide decomposition was determined. Some results are given in the following table:

Catalyst concentration $M \times 10^{-4}$	$-d[ROOH]/dt$ mole $l^{-1}/min^{-1} \times 10^{-3}$
1·53	0·127
2·59	0·132
5·56	0·202
10·54	0·400

The plot of $1/d[ROOH]/dt$ against [Cat] is linear, and thus may represent a relationship of the form

$$\frac{d[ROOH]}{dt} = \frac{1}{K - C[Cat]}$$

EFFECT OF ADDED PEROXIDE

The effect of added ethylbenzene hydroperoxide, synthesized by the method of Hock and Lang,[9] was examined in both catalyst regions. The result of adding increasing amounts of peroxide to ethylbenzene containing $6{\cdot}35 \times 10^{-5}$ M catalyst showed that the rate of oxidation progressively decreased as the initial peroxide concentration increased and tended to a final constant value. This result indicated that the peroxide formed a complex with the catalyst

$$CuSt + nROOH \longrightarrow CuSt\ nROOH$$

and that the complex had a lower activity than the uncomplexed stearate.

In the high catalyst region added peroxide also decreases the rate of oxidation, but no quantitative measurements have been made as yet.

EFFECT OF ADDING (1) Cu STEARATE (2) STEARIC ACID, AND (3) COPPER NAPHTHENATE, DURING COURSE OF REACTION

If an additional amount of catalyst was added to the reaction when in the steady state a temporary increase in rate occurs, followed by a rapid fall away to the normal value. This is exactly the behaviour to be expected when hydroperoxide is present in appreciable amounts if it complexes with the catalyst as stated in the previous section.

On adding stearic acid to a copper stearate catalysed reaction the rate was observed to pass through a well-defined maximum as the initial amount of stearate was increased.

Measurements with copper naphthenate gave similar results to copper stearate in that the catalyst showed different behaviours above and below a concentration of 10^{-4} M. Copper naphthenate was, contrary to the results observed with the paraffins,[1] a much more active catalyst, as the following data show:

Catalyst	Cat $\times 10^{-5}$ M	Max. rate (cc/min)	Total absorption mol/mol at 100 min
Cu as naphthenate	5·38	$6{\cdot}6 \times 10^{-2}$	$17{\cdot}0 \times 10^{-4}$
Cu as stearate .	6·35	$4{\cdot}1 \times 10^{-2}$	$6{\cdot}6 \times 10^{-4}$

DISCUSSION

The results so far obtained do not permit of a complete and detailed description of the course of the oxidation, and this must await the completion of the work in progress. However, the broad picture of the mechanism is clear. The copper salt-catalysed oxidation conforms to a well-established radical chain mechanism for the formation of a hydroperoxide

$$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot$$

$$RO_2\cdot + RH \xrightarrow{k_3} ROOH + R\cdot$$

This leads to the following rate law (at O_2 saturation)

$$\frac{d[ROOH]}{dt} = r_i^{\frac{1}{2}} \frac{k_3[RH]}{k_6^{\frac{1}{2}}}$$

where r_i is the rate of free radical formation (initiation). The nature of the initiation step in the copper salt-catalysed oxidation still remains obscure and does not seem to follow the simple pattern observed with the active transition metal salts. It appears most likely that the activity of the copper is associated with the reduction of Cu^{II} to Cu^{I} and the subsequent re-oxidation of Cu^{I} to Cu^{II} either by hydroperoxide or oxygen. However, it should be emphasized that the copper is never present as a bare ion but is in a highly complexed state and, as the above results on the effect of added stearic acid or ROOH show, the activity of the complex is very much determined by the nature of the groups attached to it. Also the molecular state of the catalyst is important and preliminary light scattering measurements carried out with the Bryce–Phoenix Light Scattering Photometer show clear evidence of association of the copper stearate or its complexes at high catalyst concentrations.

The initiation reaction seems to require the presence of ROOH, probably by thermal uncatalysed oxidation, as is evidenced by the elimination of the autocatalytic part of the reaction (Fig 1). Initiation, however, is not a simple electron transfer reaction between Cu^{I} or Cu^{II} complexes and the hydroperoxide,

since the experimental evidence clearly establishes that Cu^{II} itself complexes with the ROOH and that this complex has a lower activity than the copper stearate not complexed with ROOH. The existence of catalyst complexes explains the change in character of the reaction after a few per cent oxidation (Fig 2), the initial steep part of the oxygen absorption curve being due to initiation by copper complex not containing ROOH and the main linear portion being due to catalysed initiation by the Cu–ROOH complex. These possibilities may be represented as

(1) $Cu^{II} + ROOH \longrightarrow RO_2 + Cu^{I} + H^{+}$

(2) $Cu^{II} + n\text{ROOH} \longrightarrow Cu^{II}\,n\text{ROOH} \longrightarrow$ radicals

The different dependencies of the rate on the copper salt concentration which varies from $(Cu^{I})^{1\cdot0}$ to $(Cu^{II})^{0\cdot34}$ as the concentration increases also implies that the catalyst takes part in reactions other than initiation.

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MECHANISM OF COPPER CATALYSIS IN INSULATING OIL OXIDATION *

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SUMMARY

The controversy during the past few years as to whether catalysis of insulating oil oxidation by solid copper is homogeneous or heterogeneous is discussed. Evidence obtained by Panel E/Ad of ERA Sub-Committee E/A in recent collaborative investigations is presented. New light is thrown on this subject, which is important in oxidation test method development.

The results indicate that there is no contribution by a heterogeneous mechanism, and that the extent of oxidation is governed more by the ability of an oil to retain dissolved copper in solution than by its tendency to dissolve copper from the catalyst. Since only a homogeneous mechanism is operative, a correlation would be expected between the results of oxidation tests with metallic and with soluble catalysts. Such a correlation is, in fact, found to exist, and extends over so wide a range of oil stabilities that it is evident that suitable concentrations of soluble catalysts will correctly rate the oxidation characteristics of oils.

INTRODUCTION

PEOPLE have been arguing for many years about the exact way in which metallic copper catalyses the oxidation of oils. The literature on the subject is being reviewed separately in this symposium by Morton [1] and, in outlining the background to the work described in the present paper, it is therefore unnecessary to summarize more than the highlights of the controversy.

Briefly, there are two main schools of thought: the first holds that catalysis by metallic copper is primarily heterogeneous, *i.e.* that it is the metal surface itself which is the agent directly responsible for initiating reaction chains; the second that the mechanism is homogeneous, *i.e.* that the metal surface itself is not directly active, but that copper compounds are produced from it by reaction with the oil, thus finding their way into solution in the oil, and becoming the active catalytic agents in a single-phase system.

Evidence has been produced which appears, somewhat paradoxically, to support the views of both schools, and it seems possible that both mechanisms may be contributing to the catalytic process. Most authorities agree, however, that copper in an oil-soluble form is a powerful catalyst for oil oxidation, and that its use in oxidation tests can lead to shorter test durations for given levels of oil deterioration or, alternatively, to the possibility of using lower, and

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† "Shell" Research Ltd.

hence more realistic, test temperatures. Advocates of the use of soluble copper (and iron) salts in oxidation tests have based their views, initially at least, upon these undisputed facts concerning the reaction rates possible with soluble catalysts, and also upon observations which indicate the almost universal occurrence of metal dissolution in trace amounts into oils recovered from service in transformers, engines, turbines, etc.

The views of those advocating the use of soluble catalysts have been attacked on the grounds that different oils may attack metallic copper surfaces to different extents (or at different rates), producing oil-soluble copper salts at different concentrations. Hence, they allege, the use of a fixed concentration of oil-soluble copper, *ab initio*, as a catalyst might penalize unfairly those oils which are less prone to cause such attack. This possibility is referred to below, for simplicity, as the " variable corrosivity effect."

This allegation is important, especially in view of the considerable amount of collaborative work which has been, and still is, going on in Europe, and also in America, towards the development of an international oxidation test for transformer oils.

Most of the discussion on the subject has occurred during the last ten years, during which the international collaborative work has increased in tempo, following its post-war revival. The matter was only briefly touched upon in the 1946 IP symposium,[2, 3] and although the problem was fairly clearly recognized at that time, little experimental evidence was available, the consensus of opinion favouring the homogeneous mechanism. The present author associated himself with this viewpoint in an earlier paper,[4] and summarized some further evidence then available.

The argument has since developed more forcibly, and culminated during the presentation and discussion of three important and authoritative papers presented at an ASTM symposium [5] held in Cleveland, Ohio, on 17 November 1954.

In the general discussion at this symposium Clark [6] rejected the variable corrosivity effect as fallacious in the light of the results of Liander and Ericson,[7] who showed that the amount of copper taken into oil solution from a solid copper surface is not related to the tendency of the oil to undergo oxidation. Clark continued: " It necessarily follows that a given amount of soluble copper compound added to a series of oils will affect the sludge formation to a variable degree in each oil, depending on conditions not clearly demonstrated. This agrees with observations already accepted for the similar variation in the effect of solid copper on the sludging of different transformer oils."

In his reply Liander [8] presented some additional new evidence which deserves greater prominence than it has perhaps been accorded.

To summarize Liander's remarks, " not only was the rate of dissolution of metals in the oil dependent upon the characteristics of the oil, but also, moreover, on the proportions of the metal surfaces exposed to the oil, surface conditions, thickness of insulation or varnish, and many other features having no bearing whatsoever on the course of the true oxidation reaction. The use of soluble catalysts is thus logical if the object is to isolate the problem of oxidation. It remains, however, to show that by such a simplification we have not neglected any essential practical factor. Consequently we have also studied the rate of dissolution of copper in various oils. In the accompanying table (Table I) some illuminating data have been compiled for two commercial transformer oils A and B, and the series of experimental oils S1 to S5. The table contains data for the total amount of copper dissolved after 164 hours with 1 litre/hr of oxygen bubbling through 25 g of oil at 100° C calculated per unit area (100 sq. cm./25 g of oil) as an average of the experimental data in the paper.[7] The corresponding mean values of acidity and sludge have also been deduced from data in the paper in the same way, and may be compared with the acidity and sludge for the same oils oxidized with 10 p.p.m. of a soluble copper catalyst (naphthenate) instead of solid copper, but otherwise in an identical manner.

TABLE I

Comparison of Oxidation Products

Oils		A	B	S1 *	S2 *	S3 *	S4 *	S5 *
Solid copper	Corrosivity mg/sq. dm. Cu	0·2	1·0	1·0	0·2	1·2	0·2	0·1
	Acidity mg KOH/g/sq. dm. Cu	1·1	2·0	3·2	1·3	67·0	4·2	0·6
	Sludge % wt/sq. dm. Cu	0·5	1·1	1·5	0·4	36·0	0·6	0·2
Soluble copper	Acidity mg KOH/g/mg Cu	1·3	2·3	2·9	2·1	60·0	4·3	1·9
	Sludge % wt/mg Cu	0·5	0·5	1·0	0·7	39·0	0·6	0·6

* Liander's oils " S1–S5 " inclusive are identical with those designated " I.R.O. 1–5 " in the later parts of the present paper.

It is true that the rate of dissolution of copper varies appreciably for different oils. But although the over-refined oil S3 and the under-refined oils S1 and B dissolve copper more readily than the normally refined oils (A, S2, S4, and S5), the rate of dissolution for these latter oils is practically the same. As would be expected, the relation between the amounts of oxidation products for these oils is about the same with solid and soluble copper catalysts. But curiously enough, this is also the case with the other oils tested, the over-refined oil S3 as well as the under-refined oils S1 and B. For reasons not further investigated, numerical ratios of the oxidation products are almost exactly the same in both series for the same oil.

We therefore arrived at the conclusion that, in using soluble catalyst, we have not placed any oil at a disadvantage. If it is suspected that an oil is abnormal, we have recommended a special study. As an example of such a study we have cited an oil with deactivator and shown that, even in this case, soluble catalysts can be used to advantage.[11]

In the face of this strong evidence, the case for a homogeneous mechanism appears a compelling one, and it seems that the " variable corrosivity effect " is irrelevant. Yet how can this be so? How can oils oxidized with a soluble catalyst, added at a fixed concentration, produce almost exactly the same proportions of oxidation products as they do with a solid catalyst when that solid catalyst dissolves to different extents in each oil?

One possible reason is that in addition to differing in the degree to which they dissolve copper, oils might also differ in their tendency to " precipitate out " (or otherwise deactivate) part of the copper that does dissolve, so that the alignment of the two sets of results with solid and soluble catalysts could be explained. Unfortunately Liander and Ericson [7, 8] provide little information on this point.

This is one of the aspects that is examined in the present paper.

In the above-mentioned ASTM discussion Clark [6] raises other important questions: " Is solid surface catalysis satisfactorily excluded, and is the greater catalytic effect of the so-called soluble catalyst not traceable to the greater surface effect of its oil-suspended soap and later the greater surface area of the flocculated metal compound? "

These, then, are the issues which have been investigated in a collaborative research programme during the course of the last two years by three (Lobitos Oilfields Ltd, " Shell " Research Ltd, and C. C. Wakefield and Co. Ltd) of the industrial laboratories participating in the work of Panel E/Ad of the ERA. This Panel is charged with the responsibility of co-ordinating the work of a number of universities and industrial firms on the fundamentals of hydrocarbon and oil oxidation. In addition to collecting together the results of this programme, the present author has also drawn upon data obtained from the work of Panel E/Ab (see Gossling [9]), and from results obtained in other studies in his own laboratory (Thornton Research Centre).

EXPERIMENTAL

A first essential for our investigations was a reliable method of analysis for trace amounts of copper, which would be reasonably accurate in the 0·1–10-p.p.m. range. Such a method, the accuracy of which may be even better than 0·1 p.p.m. when extreme precautions are taken regarding reagent purity and atmospheric contamination, is described in Appendix A. It has been applied not only to the analysis of oils but also of the oxidation sludges derived from them.

Although some exploratory work had been done earlier, the collaborative study of this problem began effectively following a meeting of ERA Panel E/Ad at Birmingham University on 8 May 1956.

Several series of experiments have been conducted, all involving the use of the International Electrotechnical Commission (I.E.C.) oxidation test procedure described by Gossling.[9] In all of these the reaction temperature has been fixed at either 100° C or 110° C, and a variety of catalytic conditions has been investigated, with appropriate test durations being chosen so that, wherever possible, measurable quantities of sludge and acidity were obtained.

The catalysts used were:

Copper Wire, ASTM D.943–54 and D.1314–54T type, prepared according to the method instructions,[9] and used in amounts to give a variety of surface areas up to nearly 13 times that called for in the standard IEC oxidation test (9·73 sq. cm.). The former wire (1·6 mm dia) was inadvertently used in some of the experiments (results in Tables II and III) instead of the latter (1·0 mm dia), which is specified in the IEC test. In all cases, however, the results are reported on the basis of the area of copper surface used.

Copper Naphthenate, prepared from a distilled and de-oiled fraction of naphthenic acids. The copper content is 6·80% wt, and the catalyst used is from the same batch from which samples have been distributed on a world-wide basis to all the IEC investigators.

Iron Naphthenate. The details are the same as those for the copper salt, except that the metal content is 5·82% wt (Fe).

Oils

Descriptions of the oils used in the investigations are listed below, and their physical characteristics and chemical properties are summarized in Appendix B. The I.R.O. series of oils was specially prepared for the international investigations involved in the development of the IEC oxidation test, so as to represent a wide range of oil types, and consequently of oxidation stabilities. These oils were refined in various ways, in some cases from different raffinates, as indicated below, but were all derived from the same crude source. The first five are identical with the samples designated S1–S5 included by Liander and Ericson [7] in their studies. All six oils in the I.R.O. series have also been used by Ward [10] and Childs [11] in their investigations of the oxidation characteristics of insulating oils.

Insulating Reference Oil No. 1. A raffinate or solvent-refined feedstock from which transformer oils are normally produced by further oleum and earth treatment.

Insulating Reference Oil No. 2. An experimental oil produced by a combination of solvent extraction and acid-treatment, the degree of refining being somewhat less than in the case of I.R.O. 3 and I.R.O. 4.

Insulating Reference Oil No. 3. Normal transformer oil which has been more heavily solvent-extracted than I.R.O. 4.

Insulating Reference Oil No. 4. Normal transformer oil which has been less heavily solvent-extracted than I.R.O. 3.

Insulating Reference Oil No. 5. Normal transformer oil of higher aromatic content than I.R.O. 3 and I.R.O. 4.

Insulating Reference Oil No. 6. A technical white oil produced by heavy oleum treatment of a solvent-refined stock.

British National Reference Oil GB II. This oil has been selected as a British national reference oil for use in the IEC studies, and as such it replaces the sample WBD.8008, the first British reference oil contributed for the international test method development work. It meets the British specification for transformer oils (B.S. 148 : 1951), and is now being used, throughout Europe, as representative of the type of oil, commercially available in the U.K., which has given satisfactory performance in service over a long period of years.

RESULTS

(1) *First Series of Experiments*

The first series of experiments was designed to explore the extent to which copper dissolved from the metal catalyst during the standard IEC oxidation test at 100° C. The oil used was I.R.O. 5, and the series of experiments consisted of two parts:

(*a*) The first set of experiments involved separate oxidations for various intermediate test durations (of about 1, 2, 3, and 4 days, as well as the normal 164 hours duration), conducted under the standard conditions, but the catalyst wire in each test was weighed before and after the oxidation in an attempt to estimate gravimetrically the rate and extent of copper dissolution. The oxidized oils were examined after dilution with *n*-heptane for sludge and acidity in the normal way.

(*b*) In the second set of experiments, the oxidized oil samples were allowed to cool in the dark for 2 hours and then filtered, without the dilution normally employed, through a weighed ashless filter paper. The sludge was washed with *n*-heptane until it was oil-free (the washings being rejected), and weighed. The copper catalyst was weighed before and after test and the weight change recorded. The filtered oxidized oil samples were analysed for their content of dissolved copper at the various test durations. No attempt was made, in this second set of experiments, to measure the acidities of the filtered oils.

The results can be summarized briefly as follows.

In all the experiments a small but significant gain in weight of the catalyst was observed. At the shortest test duration (23 hours), this averaged 0·3 mg, and at the longest test duration (164 hours) 0·7 mg. The changes were not very regular as the test duration increased (this is not surprising in view of the smallness of the weight changes observed), but it appeared that the gains in weight were greater at longer test durations. In no single case out of twelve experiments was there a loss in weight of the catalyst. These results were rather surprising, especially when it was found that copper was present in all the filtered oxidized oil samples (*i.e.* at all test durations) in amounts up to 0·5 p.p.m. It is unlikely that the gain in weight of the catalyst was due to adherent sludge from the oxidized oil; similar effects have been observed by Wilson and Garner [12] in their investigations of the role of peroxides in the corrosion of lead by lubricating oils, and it is assumed that a surface layer of oxide on the metal is responsible.

The amounts of oil-insoluble sludge were exceedingly small (although sludge was visible on the filter paper) and so near to zero that small positive or negative weight changes of the filter paper were ignored. No attempt was made to detect copper in the sludges in these preliminary experiments, although, as will be seen later, with the improved techniques that became available, the copper present in such sludges is by no means negligible, and in fact represents an important part of the total dissolving from the metal.

(2) *Second Series of Experiments*

In the second series of experiments an attempt was made to achieve greater extents of oxidation and more measurable amounts of dissolved copper. The experiments outlined above were repeated with larger surface areas of copper wire (up to nearly 13 times the standard IEC catalyst area, this being the largest amount that could conveniently be compressed into the reaction vessel, and still contact the entire oil sample), and at a temperature of 110° C as well as 100° C. A single oil (again I.R.O. 5) and one test duration (164 hours) only were used. Since these experiments were of a purely exploratory nature during the period in which the techniques were being worked out, the results are not quoted in detail,* although their general pattern is of interest, and led to a considerable extension of the investigations. From the results, it became clear that a small amount of copper does dissolve in the oxidizing oil, most of it precipitating out again in the oil-insoluble † sludge.

At this stage of the investigations, before our techniques had been perfected, the amounts of copper

* More accurate results became available subsequently, when the studies were extended to a variety of oils. The results are summarized later.

† Not necessarily the same material as the heptane-insoluble sludge which is usually formed in rather larger amounts in the standard test involving dilution/precipitation with *n*-heptane.

present in the filtered oils and sludges did not show a regular dependence on the surface area of copper catalyst, as might have been expected from the work of Liander and Ericson.[7] However, in the case of the tests at the higher temperature (110° C), as the catalytic area was increased, there appeared to be rather less copper present in the filtered oils and rather more in the sludge. In general, at both temperatures a total of about 1–2 p.p.m. of copper found its way into the oxidized oil. Of this, the greater proportion was usually present in the sludge.

As regards sludge and acidity formation, both were dependent to some extent on the catalytic surface area used. It was, however, clear that doubling, trebling, and quadrupling the copper surface area by no means caused corresponding increases in the amounts of oxidation products formed. In the 100° C test there was evidence that with the largest amounts of catalyst the sludge value was becoming independent of the catalyst area, whilst in the 110° C tests the same feature was observed in the acidity figures. The 10° C higher temperature caused a 200–300 per cent increase in the sludge levels, but a much smaller increase (50 per cent or less) in the acidity levels. It was clear that these greater rates of oxidation were not directly associated with the increased dissolution of the metal, but were largely the result of thermal effects.

A comparison of these results in conjunction with others obtained using exactly the same test conditions but with a soluble copper catalyst (naphthenate at 0·5, 1, and 2 p.p.m.) in place of the metallic copper led to some interesting conclusions. It appears that, at 100° C, metallic copper (which dissolves in the oil to such an extent as to be comparable in its total concentration to the amounts of soluble catalyst deliberately added in these experiments) causes 5–10 times as much sludge formation and 3–5 times as much acidity development as the soluble catalyst. At 110° C the ratios are 6–13 times (sludge) and 3–4 times (acidity).

At this stage of the investigations it looked as though solid copper had a more powerful catalytic effect than could be accounted for solely by the activity of deliberately added amounts of soluble copper corresponding to those which become dissolved and/or precipitated in the sludge. In other words, there seemed to be some evidence for the existence of a heterogeneous mechanism of catalysis, as well as a homogeneous one.

There was, however, uncertainty as to how much of the deliberately added soluble copper remained in the oil as an active catalyst. Even at these low levels of soluble copper concentration, a major part of the added copper could well have been precipitated very rapidly into the sludge, where it might have little or no catalytic activity. These observations were considered to be sufficiently important to warrant further and more extensive investigations. If it could be proved that metallic copper was substantially more active catalytically than could be accounted for on the basis of the amounts of copper dissolving from it, then this would point to a predominantly heterogeneous mechanism.

During the course of this second series of experiments, it became evident that more consistent results were obtained with a sintered glass filter (grade 4 porosity) than when ashless filter papers were used to collect the sludge for analysis. In most cases the actual weight of sludge was too small to be measured, and the crucible itself was extracted directly for the analysis, the copper content of the sludge being calculated on the basis of the original oil weight. Other improvements in the technique were also made during this period, and these are incorporated in the method given in Appendix A.

(3) *Third Series of Experiments*

This involved a repetition of the earlier work, using the more refined analytical technique, but with the complete range of oils described in the "Experimental" section. The temperature used was 110° C, and the test duration was, in all cases, 164 hours. Metallic copper catalyst only was used, with a wide range of surface areas (zero—*i.e.* no copper at all, 15·6, 31·2, 62·4, 94·6, and 124·8 sq. cm.). The greatest of these is 12·8 times the area specified in the standard IEC oxidation test (9·73 sq. cm.). and corresponds to the maximum amount of the wire that can be conveniently packed into the reaction vessel and still be in contact with the entire oil sample.

As in the first and second series of experiments, two sets of oxidation tests were conducted, the first set under the standard IEC oxidation conditions (except for catalyst area and temperature, 110° C) solely for the purpose of measuring sludges and acidities, and the second set without the usual heptane-dilution step (*i.e.* direct filtration of the oxidized oil) with the object of measuring the distribution of copper between the filtrate oil and the oil-insoluble sludge.

The results of the first set of oxidations in this third series of experiments are summarized in Table II.

For all but two of the oils tested (I.R.O. 3 and 6), the sludge and acidity results are strongly dependent on the surface area of copper catalyst used. The dependence is most marked in the region of the catalyst area specified in the standard IEC test (see Figs 1 and 2), but for most of the oils becomes less with increasing catalyst area. In this connexion, it is noteworthy that Massey [13] has observed that, in the British oxidation test for transformer oils (IP 56; B.S. 148 : 1951), the conditions are so chosen as to ensure that the oils are tested under conditions of maximum catalysis (*i.e.* an increase in catalyst area causes no further oil oxidation). Solid metal surfaces of this kind are notoriously difficult to clean reproducibly by

TABLE II

*Sludge and Acidity Results in the IEC Oxidation Test * over a Wide Range of Catalyst Areas*

Catalyst \ Oil		I.R.O. 1		I.R.O. 2		I.R.O. 3 †		I.R.O. 4 †		I.R.O. 5		I.R.O. 6 †		GB II	
Surface area, cm²	No. of times standard I.E.C. catalyst area	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt
0	0	0·17	0·01	0·11	0·00	21·25	11·38	0·55	0·01	0·06	0·00	21·23	14·25	0·11	0·01
15·6	1·6	0·90	0·65	0·45	0·22	21·35	16·40	1·83	0·49	0·17	0·06	21·23	15·90	0·28	0·15
31·2	3·2	1·12	0·79	0·56	0·39	20·8	17·03	2·77	0·91	0·28	0·11	22·75	17·58	0·40	0·19
62·4	6·4	1·35	1·13	0·67	0·52	20·8	19·47	4·05	1·50	0·44	0·18	23·20	19·73	0·39	0·20
93·6	9·6	1·44	1·32	0·67	0·58	21·25	23·42	6·08	3·50	0·50	0·25	23·20	20·02	0·50	0·25
124·8	12·8	1·55	1·41	0·78	0·61	20·0	23·66	6·62	3·46	0·53	0·28	23·63	22·65	0·67	0·33

* Conditions: 110° C, Cu-wire catalyst, 164 hours.
† The oxidized oil was a brown jelly, and was difficult to mix with cold *n*-heptane. The mixture was therefore warmed slightly, allowed to cool, with overnight standing, and the heptane/oil layer decanted. The residue was chloroform-extracted and worked up in the usual way. Additional alcohol was required for homogeneity of the titration mixture.

abrasives, which act by scratching away the surface layers (these may be partially oxidized), leaving behind a variable and ill-defined surface area of highly indented bright metal. In all the present work the catalyst areas quoted are minimum ones, no allowance having been made for the additional area introduced by the surface roughness produced during the cleaning process.

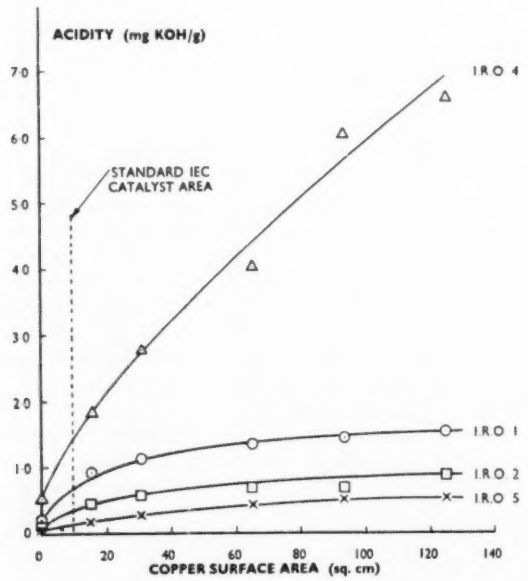

FIG 1

OXIDATION AT 110° C; 164 HOURS; VARIOUS AREAS OF SOLID COPPER CATALYST; ACIDITY RESULTS

The location of the IEC catalyst area in the region where small changes in area have the largest effect on the results is a possible cause of some, at least, of the discrepancies observed in the results obtained by different laboratories in collaborative work with the IEC oxidation test. The possibility of improving the cleaning process, perhaps by the substitution of chemical cleaning methods, undoubtedly merits further investigation.

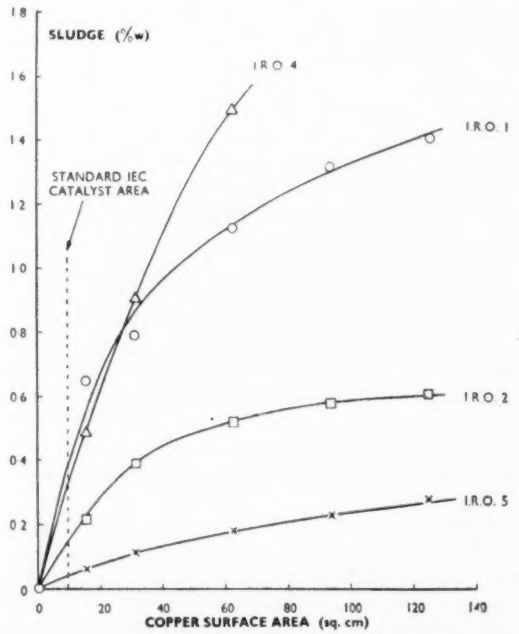

FIG 2

OXIDATION AT 110° C; 164 HOURS; VARIOUS AREAS OF SOLID COPPER CATALYST; SLUDGE RESULTS

Although the dependence of the amount of oxidation products on catalyst surface area is of the same general pattern for all but two (I.R.O. 3 and 6) of the oils examined, there are marked differences in the catalyst areas where the dependence becomes less critical. (In fact, the oxidation results with I.R.O. 4 are still rather strongly dependent on catalyst area even in the most extreme tests conducted.) Because

of this, it would seem to be possible for the merit-ratings of two oils to be reversed in tests conducted with different catalyst surface areas.

The two oils (I.R.O. 3 and I.R.O. 6) which have quite different " catalyst response " curves from the remainder have both been heavily refined and have low aromatic contents. Even in the uncatalysed tests, they produce copious amounts of sludge and develop very high acidities. In fact, all the catalyst areas used have virtually no effect on the acidity development in these oils. There is, however, some effect of catalyst area on the amount of sludge produced, which tend to increase with catalyst area, gradually becoming less dependent at the highest levels used.

oil GB II are perhaps slightly more accurate than those for the remaining oils, and show a slight increase only in dissolved copper content with increasing catalyst area. With the remaining oils (I.R.O. 1, 3, 4, and 6), there is definite evidence that more soluble copper finds its way into the oils at the higher catalyst areas (see Table III and Figs 4–6). These are the four oils the extent of oxidation of which appears to continue increasing with catalyst surface area up to the largest areas used. The remaining oils appear to reach their maximum extent of oxidation at rather smaller catalyst areas, except perhaps for GB II, where the tendency is again for it to be intermediate between the two groups of oils.

The amounts of copper appearing in the insoluble

TABLE III

Dissolution of Copper in the IEC Oxidation Test * *(Distribution in p.p.m.† between Oil and Sludge)*

Catalyst \ Oil		I.R.O. 1			I.R.O. 2			I.R.O. 3			I.R.O. 4			I.R.O. 5			I.R.O. 6			GB II		
Surface area, cm²	No. of times standard I.E.C. catalyst area	Oil	Sludge	Total	Oil	Sludge	Total	Oil	Sludge	Total	Oil	Sludge	Total	Oil	Sludge	Total	Oil	Sludge	Total	Oil	Sludge	Total
0	0	0·1	0	0·1	0·4	0	0·4	1·5	0·3	1·8	0·8	0	0·8	0	0	0	1·9	1·6	3·5	0·16	0·28	0·44
15·6	1·6	1·4	8·0	9·4	0·7	1·4	2·1	2·2	2·9	5·1	1·8	0·5	2·3	0·6	0·9	1·5	2·6	3·6	6·2	0·11	0·7	0·8
31·2	3·2	2·0	16·0	18·0	0·3	1·6	1·9	3·0	3·5	6·5	1·2	0·5	1·7	0·6	1·0	1·6	2·7	5·2	7·9	0·20	1·3	1·5
62·4	6·4	2·4	23·0	25·4	0·9	6·8	7·7	3·6	9·0	12·6	1·6	1·0	2·6	0·1	1·2	1·3	2·9	8·1	11·0	0·31	1·7	2·0
93·6	9·6	3·2	31·0	34·2	0·3	9·0	9·3	3·8	11·0	14·8	1·7	1·1	2·8	0·6	2·6	3·2	3·2	15·9	19·1	0·36	2·8	3·2
124·8	12·8	4·0	47·0	51·0	0·5	10·1	10·6	5·3	18·4	23·7	1·8	1·2	3·0	0·1	1·6	1·7	5·3	27‡	32·3‡	0·44	2·3	2·7

* Conditions: 110° C, Cu wire catalyst, 164 hours, no dilution. † Calculated on basis of initial oil quantity. ‡ Estimated graphically.

An important general observation is that, taking the overall results with all the catalyst surface area into account, the seven oils studied are rated in the same order of merit (see Table IV and Fig 3) regardless of whether sludge or acidity is used as the criterion. This conclusion is interesting, especially in view of the wide range of oil types represented in this series of experiments. It holds generally over all the catalyst areas studied, but comparisons of the results obtained with any two individual catalyst areas show that some reversals of the merit-ratings of the different oils do occur.

The results of the second set of experiments in this third series, made with the object of studying the extent and nature of copper dissolution, are summarized in Table III.

The amounts of copper dissolving from the catalyst and remaining in the soluble form in the oil are generally small in comparison with those appearing in the insoluble form in the sludge, and are much less dependent on the catalyst surface area. In fact, in the case of I.R.O. 2 and 5, the amounts present in the soluble form appear to be independent of the catalyst area, provided that this is not zero. The results for

form (*i.e.* in the sludge) are in all cases markedly dependent on the catalyst area used. They have been calculated on the same basis as the oil-soluble copper contents (*i.e.* parts Cu per million of original oil weight before oxidation). Up to 5·3 p.p.m. has been found in two oxidized oils (I.R.O. 3 and 6) in the soluble form, whereas up to 47 p.p.m. is present in the sludge produced by another oil (I.R.O. 1). In only one case (I.R.O. 4) was significantly more copper found in the soluble form than in the insoluble form, this observation holding good for all the catalyst areas used.

The total amounts of copper (*i.e.* soluble plus insoluble) dissolving from the catalyst and appearing in the oxidized oil and sludge range from 0·8 to 9·4 p.p.m. at the smallest catalyst surface area used, and from 1·7 to 51 p.p.m. at the largest. A surprising feature is that in the uncatalysed tests (Table III) some copper was found in either the filtered oil or the sludge or both, with one exception (I.R.O. 5). The largest amount was present in I.R.O. 3 and 6, the two most highly refined oils, and it must be assumed that this copper was present as a contaminant, either initially in the oils or picked up during the course of the oxidation tests. (The accuracy of the copper determina-

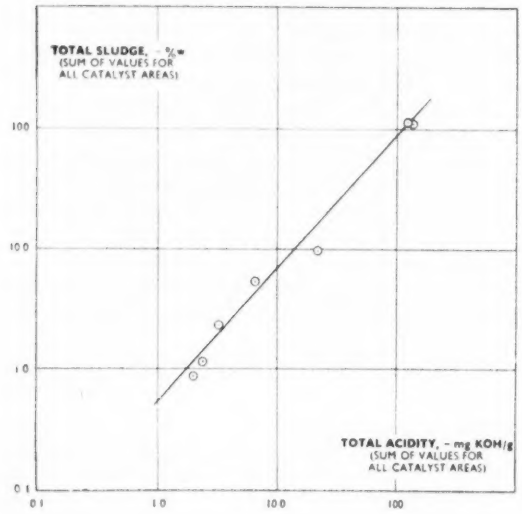

FIG 3

RELATION BETWEEN OVERALL SLUDGES AND ACIDITIES

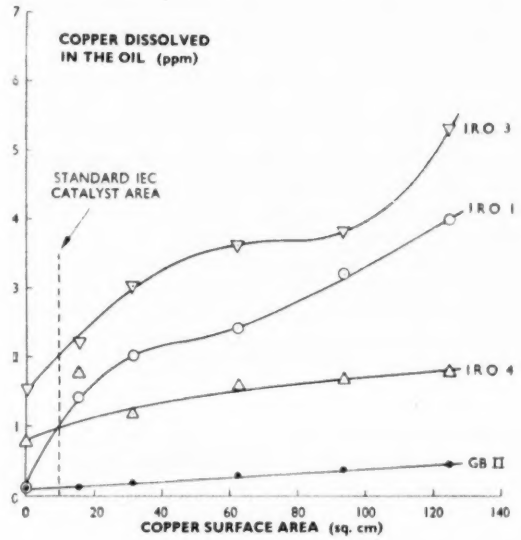

FIG 4

EXTENT OF DISSOLUTION OF COPPER IN METAL-CATALYSED OXIDATION AT 110° C; 164 HOURS; SOLUBLE COPPER CONTENTS

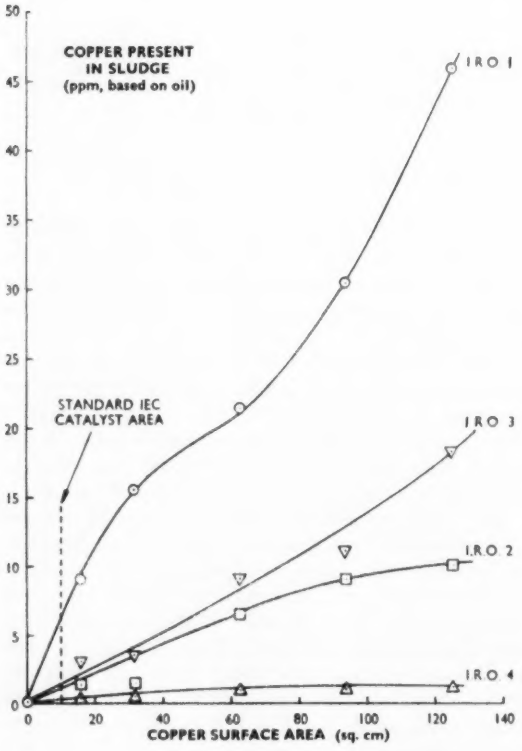

FIG 5

EXTENT OF DISSOLUTION OF COPPER IN METAL-CATALYSED OXIDATION AT 110° C; 164 HOURS; COPPER APPEARING IN SLUDGES

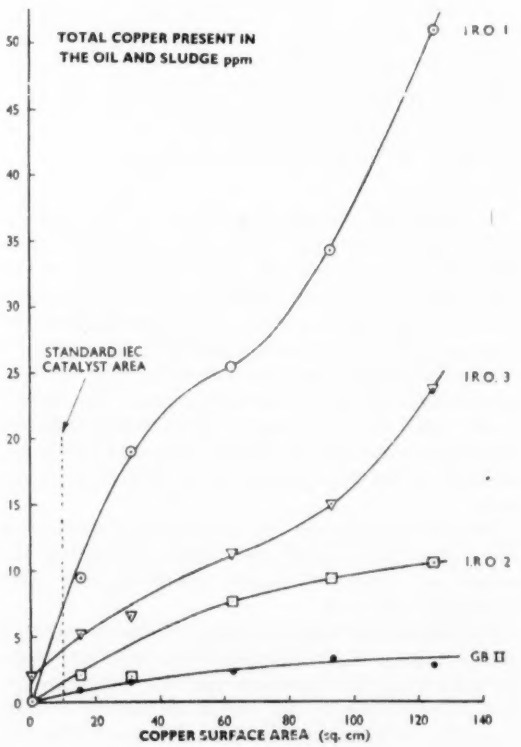

FIG 6

DISSOLUTION OF COPPER IN METAL-CATALYSED OXIDATION AT 110° C; 164 HOURS; TOTAL COPPER CONTENTS

tions is believed to be at least as good as 0·5 p.p.m., and in one case—GB II results—may be about 0·05 p.p.m.).

A most important conclusion emerges from a study of Table IV, which summarizes in a convenient form the merit-ratings of the oils in terms of sludge formation and acidity development, and their tendencies to retain copper dissolved from the catalyst in the soluble form in the oil or reject it into the sludge. This is that a correlation exists between the sludge or acidity merit-rating and the total amounts of copper

TABLE IV

" Merit-Ratings " of Oils

	Best						Worst
Acidity:	5	GB II	2	1	4	3	6
Sludge:	5	GB II	2	1	4	3	6
	Least						Most
Soluble copper in oil (totals over all catalyst areas) . . .	GB II	5		4	1	6	
Insoluble copper in sludge (totals over all catalyst areas) . . .	4	5	GB II	2	3	6	1
Copper in oil + sludge (overall totals) . .	5	GB II	4	2	3	6	1

found to be present in the soluble form in the oxidized oil. The only reversals of merit-rating are between adjacent oils. Similar correlations hold over each of the catalyst areas studied, and although none of them is perfect, the general trend is highly significant. The overall correlation is illustrated in Fig 7, where each point represents a summation of the data for all catalyst areas.

From Table IV it can be seen that there is also a general tendency for the amounts of oil-soluble copper to be loosely related to the amounts appearing in the sludge, although this is less well established. Furthermore, there is little evidence of a relationship between the merit-ratings of the oils and the total copper (soluble plus insoluble) present in them, although a general trend in this direction is still discernible.

It is encouraging to note that although Liander and

TABLE V

Corrosivity Data

Oil	I.R.O. 1	I.R.O. 2	I.R.O. 3	I.R.O. 4	I.R.O. 5
Liander and Ericson [8]					
Overall average (mg/dm²) for Fig 6 data [7] (totals, *i.e.* soluble plus insoluble) .	1·0	0·2	1·2	0·2	0·1
Data from Present Work					
Overall total (p.p.m.) soluble copper, remaining in the soluble form . . .	13·1	3·1	19·4	8·9	2·0
Overall total (p.p.m.) soluble plus insoluble . .	138·1	32·0	64·5	13·2	9·3

Ericson's data [7, 8] (see Table I) were obtained under rather different experimental conditions from our own, the corrosivity observations for the oils tested in both investigations are in broad alignment (Table V).

Summing up the conclusions from this phase of the investigations, it can be stated that oils differ greatly in their tendency to dissolve copper from a solid catalyst, and also in their ability to reject various proportions of that dissolved into an insoluble form in the sludge. It is the amount remaining in the dissolved form which appears to govern both the acid-forming and sludge-forming propensities of the oils to a predominant extent. To take but a single example, one oil (I.R.O. 2) dissolves up to three times as much

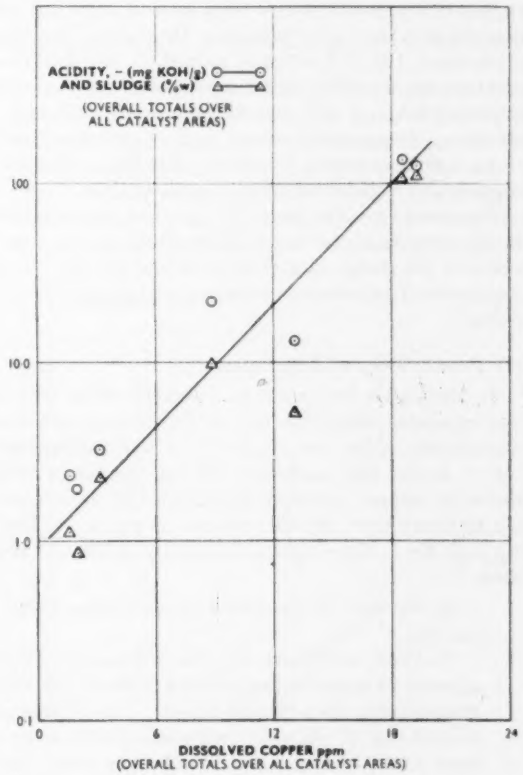

FIG 7

RELATION BETWEEN EXTENT OF OXIDATION IN METALLIC-COPPER CATALYSED TESTS AND DISSOLVED COPPER CONTENTS AT THE END OF TEST

copper from the solid catalyst as another oil (I.R.O. 4), but rejects so much of it into the insoluble form in the sludge that the amount remaining in the soluble form is only about one-third of that present in the soluble form in I.R.O. 4. The merit-rating of I.R.O. 2 in terms of sludge- and acid-formation is consequently markedly superior to that of I.R.O. 4.

What factors are responsible for such differences amongst oils? Looking at the results in conjunction with the data for aromatic content (Appendix B) and the degrees of refining of the oils (see earlier), it appears that the oils of low aromatic content (high degree of refining), *e.g.* I.R.O. 3 and 6, dissolve a lot

of copper, and although they reject a large proportion of it into the sludge, the amount left in the soluble form in the oil is more than that in the other oils. Oils such as I.R.O. 2, 5, and GB II with a more normal degree of refining, and higher aromatic contents, do not dissolve nearly so much copper from the catalyst and reject a very large proportion of what they do dissolve into the insoluble form in the sludge. I.R.O. 4 with an aromatic content (9·8% wt) intermediate between these two classes of oil does not dissolve much copper either, but it rejects very little of what it does dissolve into the insoluble form in the sludge. On the other hand, I.R.O. 1, a lightly refined oil, dissolves the most copper, and although it rejects about 90 per cent into the sludge, it still retains a fair concentration in solution. It appears therefore that oils manufactured to an optimum degree of refining dissolve very little copper, and reject most of it into the sludge.

Two questions now arise: (*a*) to what extent is the sludge soluble in the hot oxidizing oil? (*b*) to what extent is the sludge catalytically active, if at all? The next series of experiments was designed to answer these points.

(4) *Fourth Series of Experiments*

To investigate the extent to which the sludge which was separated under the normal filtration conditions was soluble in the hot oil, I.R.O. 5 was oxidized at 110° C in the IEC oxidation test for 164 hours with the solid copper catalyst (standard IEC area) and for 48 hours with soluble catalyst (5 p.p.m. Cu and 5 p.p.m. Fe). Three sets of filtration conditions were used:

(*a*) Normal (*i.e.* dilution with *n*-heptane, standing, etc.).

(*b*) Cold, undiluted (*i.e.* the oxidized oil was allowed to stand in the dark for 2 hours at room temperature, then filtered direct. The filter was sucked dry of oil, and then washed with *n*-heptane until oil-free. The sludge was then dissolved in chloroform, and the sludge recovered in a separate weighed vessel).

(*c*) Hot, undiluted (as under (*b*), but the hot oxidized oil was transferred immediately at the end of the test to a hot filter and filtration conducted as rapidly as possible).

The results can be summarized briefly as follows. The sludge recovered by cold filtration of the undiluted oil amounted to about three-quarters of that recovered in the standard method using heptane-dilution. That recovered by hot filtration of the undiluted oil amounted to only about half that obtained in the standard method. Hence it can be concluded that, for this oil at least, the sludge formed during the oxidation is more soluble in the hot oil than in the cold oil, and that *n*-heptane precipitates from the cold oil a small additional quantity of insoluble material.

Next, twelve separate oxidation tests were made using the same oil (I.R.O. 5), with 10 p.p.m. soluble copper, at 110° C for 48 hours, with the sole object of collecting the oil-insoluble sludge formed. This was bulked and homogenized and, upon analysis, found to contain 0·682% wt copper. This sludge was then added back to fresh samples of I.R.O. 5 in amounts corresponding to the addition of 1, 2, 5, and 10 p.p.m. added copper. A series of 48-hr tests at 110° C was then conducted. The results of these, by comparison with those of uncatalysed tests, and of tests catalysed by the addition of soluble copper (see later), showed that the sludge obtained under these conditions was completely without catalytic effect. (In all the tests the acidity was about 0·05 mg KOH/g, and the sludge 0·01% wt or less.)

(5) *Fifth Series of Experiments*

It was next decided to investigate the catalytic effects of deliberately added soluble copper in the various oils at concentrations around those found to be present in the oils after tests using metallic copper catalyst. The object was to try to relate the extent of oxidation under the two sets of conditions, metallic- and soluble-copper-catalysed. Knowing the amounts of copper dissolved from the metallic catalyst, we could then assess whether there was any evidence for a contribution by a heterogeneous mechanism by comparing the extents of oxidation at similar soluble copper catalyst levels under the two sets of conditions. The tests were conducted for 164 hours at 110° C, and the soluble copper was added at concentrations of 0·5, 2·5, 5·0, 10·0, and 50·0 p.p.m. An uncatalysed oxidation test was also run at the same time on each oil. The results are summarized in Table VI.

First, the extent of oxidation in these tests with soluble copper over the 0·5–10·0 p.p.m. range is, on the whole, less than that with large areas of metallic copper, other conditions of time and temperature being the same. Some typical catalyst response curves are plotted in Figs 8 and 9. (Not all the available results are plotted, because in some cases the curves for similar oils would overlap and confuse the general picture.)

An important point is that the curves sometimes intersect one another at different levels of soluble copper concentration, which means that a comparison of the oils at one catalyst level would result in a different merit-rating from that obtained by a comparison at another level. Clearly, at the highest soluble copper concentration used the oils are rated in a quite different order from that obtained with metallic copper. For example, under these conditions (50 p.p.m.), I.R.O. 1 appears to be a more oxidation-stable oil than I.R.O. 5, a state of affairs which is clearly suspect, since it is the reverse of that found in any of the national oxidation tests to which these oils were subjected (see Appendix B).

TABLE VI

Effect of Various Soluble Copper Concentrations in the IEC Oxidation Test *

Soluble catalyst concentration, p.p.m. Cu \ Oil	I.R.O. 1		I.R.O. 2		I.R.O. 3 †		I.R.O. 4		I.R.O. 5		I.R.O. 6 †		GB II	
	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt	Acidity, mg KOH/g	Sludge, % wt
0	0·15	0·01	0·10	0·00	19·65	7·73	0·55	0·00	0·05	0·01	22·04	10·86	0·11	0·00
0·5	0·31	0·01	0·15	0·01	20·84	11·21	0·71	0·25	0·10	0·01	20·80	11·31	0·36	0·02
2·5	0·62	0·18	0·44	0·19	19·22	11·32	1·38	0·27	0·21	0·07	21·42	11·85	0·42	0·11
5·0	0·73	0·31	0·63	0·25	20·09	12·63	1·64	0·34	0·36	0·12	20·40	11·54	0·50	0·14
10·0	0·94	0·51	0·83	0·37	18·56	11·47	1·78	0·45	0·52	0·22	20·60	11·03	0·67	0·19
50·0	1·51	1·13	1·39	1·04	19·87	12·40	4·91	1·85	1·88	1·23	20·70	12·05	2·19	1·36

* Conditions 110° C, soluble copper only, 164 hours.
† Sludge was resinous, and had to be chloroform-extracted. In the acidity determination additional alcohol was required for homogeneity of the titration mixture.

However, at lower soluble catalyst concentrations the results are in much closer alignment with those of the metal-catalysed tests * (*cf.* the 10 p.p.m. soluble-copper-catalysed test results in Table VI with the

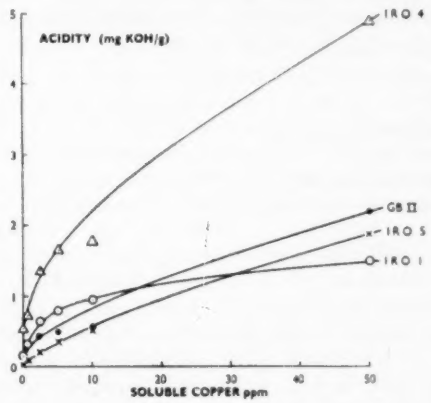

FIG 8

EFFECT OF SOLUBLE COPPER CONCENTRATION ON ACIDITY DEVELOPMENT AT 110° C; 164 HOURS

15·6 sq. cm. area metallic copper ones of Table II), although the agreement for individual oils is by no means exact. As an illustration, at the smallest area of copper surface used (15·6 sq. cm.), I.R.O. 1 produces more acidity and sludge than with 2·5 p.p.m. added soluble copper, whilst I.R.O. 5 produces almost the same amounts under both sets of catalyst conditions. However, with this area of solid catalyst, the amounts of soluble copper present in the two oils at the end of test are 1·4 and 0·6 p.p.m. respectively. Hence, if the soluble copper content alone is responsible for the metallic copper catalysis (*i.e.* if there is no contribution from a heterogeneous mechanism), then in order to account for the results obtained with the soluble catalyst added at 2·5 p.p.m., about three-quarters at least of this amount would have to be precipitated in an inactive form at an early stage in the oxidation process.

It is important to note that the soluble-catalysed test results agree fairly well with those of the metal-catalysed tests when the comparisons are made at a soluble catalyst level similar to the total (*i.e.* soluble plus insoluble) copper content found in the metal-catalysed tests. As indicated above, the agreement is poor when the comparison is made solely on the

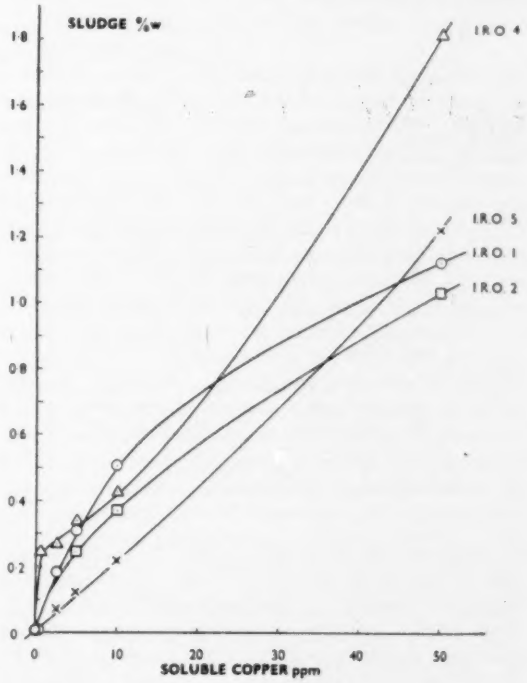

FIG 9

EFFECT OF SOLUBLE COPPER CONCENTRATION ON SLUDGE FORMATION AT 110° C; 164 HOURS

basis of the final soluble copper content (metal-catalysed tests) and initial added soluble copper content (soluble catalysed tests). For all the oils, the metal catalyst appears to be more active than the

* For example, the 5 p.p.m. soluble copper results place the oils in the same order of merit as the metal-catalysed tests (see Table IV).

soluble one (at an initial level of dissolved copper comparable with that appearing in the metal-catalysed test).

To summarize, two explanations are possible: (*a*) that there is a significant degree of heterogeneous catalysis by metallic copper; (*b*) that in the soluble-copper-catalysed tests a proportion—perhaps a very substantial one—of the initially dissolved copper is precipitated out from solution into a non-catalytic form at an early stage. If the extent of precipitation of the copper from the soluble catalyst is, in fact, large, then the possibility can be ruled out of there being a significant contribution from a heterogeneous catalysis mechanism with the solid catalyst. The next series of experiments was designed to investigate this point.

(6) *Sixth Series of Experiments*

The object of this series was to see how much copper comes out of solution from a soluble-copper-catalysed oil blend during oxidation at 110° C, and also how soon precipitation occurred during the normal 164 hours test duration. A comparison of the results with those of the metallic-copper-catalysed tests should enable an answer to be given to the question raised by the fifth series of experiments: " Is there a significant contribution from a heterogeneous catalysis mechanism in the metal-catalysed tests? "

To investigate this, a collaborative inter-laboratory programme was started involving 54 oxidation tests on six oils (I.R.O. 6 was omitted from this particular study, partly because of its similarity to I.R.O. 3, and partly for convenience in the design of the experiment). The programme was statistically designed to cover three concentrations of soluble copper catalyst (2·5, 10·0, and 50·0 p.p.m.), and three test durations (1, 24, and 164 hours). The oxidations were all conducted at 110° C, and the oxidized oils were filtered without dilution with *n*-heptane, after they had been allowed to cool for 2 hours in the dark. The heptane-washed, oil-free sludge and the filtrate oil were then analysed for their copper contents as before, the results being expressed as " p.p.m. original oil." The individual tests and analyses were shared equally amongst the three collaborating laboratories, the division being systematized so as to conform with a design to yield results amenable to straightforward statistical analysis. The results are summarized in Table VII.

It is evident that a very substantial proportion of the added soluble copper is precipitated in an insoluble form in the sludge; the effective concentrations of soluble catalyst rapidly become very low, and are of the same order as those found in the metal-catalysed oxidations. The precipitation occurs at an early stage in the oxidation tests, in all cases being virtually complete by the end of 24 hours, and even in some cases by the end of the first hour. In a few cases precipitation seems to be rather slower; in some oils no sludge (or perhaps only a trace amount) was found during the first hour of the oxidation, although extensive precipitation occurred shortly afterwards. The amounts of copper " recovered " in the oxidation products were, in general, reasonably close to the amounts deliberately added at the start of the experiments.

The results provide indisputable evidence concerning the mechanism of catalysis by metallic copper. The fact that such a large proportion of the deliberately added soluble copper was precipitated in these experiments points conclusively to explanation (*b*) of the previous section, so that in metal-catalysed oxidations the extent of the reactions can be accounted

TABLE VII

Precipitation of Copper in Soluble-Copper-Catalysed Tests *

Catalyst concentration, p.p.m.	Test duration, hours	Copper distribution (p.p.m.) amongst the oxidation products																	
		I.R.O. 1			I.R.O. 2			I.R.O. 3			I.R.O. 4			I.R.O. 5			GB II		
		O	S	T	O	S	T	O	S	T	O	S	T	O	S	T	O	S	T
2·5	1	2·2	0	2·2	0·7	1·6	2·3	0·2	2·4	2·6	0·6	2·6	3·2	3·1	0	3·1	0·9	1·6	2·5
	24	0·5	2·2	2·7	0·5	2·0	2·5	0·3	0·6	0·9	0·2	2·0	2·2	0·2	2·7	2·9	0·1	2·3	2·4
	164	0·1	1·9	2·0	0·3	2·0	2·3	0·2	2·5	2·7	0·1	2·8	2·9	0·3	2·2	2·5	1·0	1·7	2·7
10·0	1	0·3	8·6	8·9	1·6	8·2	9·8	10·3	0	10·3	0·7	8·3	9·0	0·6	9·6	10·2	10·3	0	10·3
	24	1·2	7·0	8·2	0·2	11·4	11·6	0·2	8·4	8·6	0·3	5·9	6·2	0·3	8·7	9·0	0·4	10·3	10·7
	164	1·4	8·7	10·1	0·6	10·0	10·6	0·9	9·6	10·5	0·2	10·5	10·7	0·3	8·9	9·2	0·2	7·8	8·0
50·0	1	0·4	43·6	44·0	41·4	0	41·4	27·6	19·0	46·6	8·0	34·2	42·2	5·2	41·8	47·0	14·5	36·0	50·5
	24	1·2	48·0	49·2	2·2	48·4	50·6	0·4	49·6	50·0	0·2	52·8	53·0	0·1	45·3	45·4	0·2	47·0	47·2
	164	1·7	54·0	55·7	2·5	47·5	50·0	0·7	45·6	46·3	0·3	42·1	42·4	0·9	51·9	52·8	0·4	49·1	49·5

O = Oil; S = Sludge; T = Total.

* Conditions: 110° C, duration and catalyst concentration as specified in the table; filtration undiluted, cold.

for entirely by the amounts of oil-soluble copper found. The apparent lack of correspondence in the extent of oxidation which was suspected earlier between the results under the two sets of conditions (soluble- and metallic-catalysed tests) is now seen to be due to the extensive precipitation of copper which occurs with the soluble catalyst. At equal effective soluble copper concentrations the results under the two sets of conditions are closely comparable.

(7) *Seventh Series of Experiments*

Whilst the research described above was in progress, a separate series of experiments was being conducted in an attempt to establish, by a different method, whether or not there is a contribution by a heterogeneous mechanism in the catalytic activity of metallic copper. These experiments involved a study of what happens when the metallic catalyst is removed at an intermediate point during the oxidation process. Provided the point is so chosen that there is already present in the oil a significant amount of oil-soluble copper, then, if there is an element of heterogeneous catalysis, the removal of the solid catalyst should cause an abrupt discontinuity in the oxidation rate curve, which should then correspond to a slower reaction.

Experiments were therefore made with I.R.O. 5 at 110° C with a metallic-copper catalyst (standard IEC area) to find out at what stage in the test significant amounts of copper had dissolved from the catalyst. Measurable amounts of copper were found in the sludges at 24, 48, and 96 hours, approximate values being 0·4, 0·9, and 1·3 p.p.m. (based on the weight of oil taken). The amounts found in the scluble form in the oil were smaller, but it was nevertheless decided to continue with the investigation to see what happened when the metallic copper catalyst was removed at 24 hours.

In another set of experiments not only was the copper catalyst removed but also the sludge present in the oil was removed by filtration. (The oil was allowed to cool overnight before filtering it through a filter paper.) The oxidation was then allowed to continue for a further period up to 96 hours total duration.

The duplicate results under each condition were in good agreement, but the differences between the results under the different conditions were so small as to be barely significant, the levels of sludge and acidity at 96 hours being of the order of 0·07% wt and 0·3–0·4 mg KOH/g in all cases. There was consequently no evidence of significantly less oxidation having occurred in the samples from which the catalyst has been removed; nor was there any evidence that removal of the sludge had caused a deceleration in oxidation rate. This is in line with the observations from the fourth series of experiments that the sludge itself is without catalytic effect. As would be expected, the copper contents of the sludges were substantially higher in those tests where metallic copper catalyst had been present throughout, indicating that the copper continued to pass into solution, and was then precipitated in the sludge during the entire course of the test.

Further experiments along these lines were made using a higher surface area of copper (3·2 times the IEC area, as in Table II). Greater extents of oxidation were thereby achieved, but again no evidence was obtained that copper-withdrawal at 24 hours caused a reduction in oxidation rate. In fact, there was some indication of a slightly greater extent of oxidation in the tests where the copper wire was removed. Filtration of the oil, after the copper was removed, this time caused a substantial decrease in the extent of the subsequent oxidation. Since earlier experiments have shown that the sludge filtered from this oil is catalytically inactive, there is reason to suppose that the reduced extent of oxidation is due to absorption of soluble copper on the filter; analyses of the filtered oil and sludge at the end of the 164-hours oxidation support this belief.

Similar results have been obtained by Kreulen,[14] who found that the removal of copper (in amounts varying from 1·25 to 10 g/250 ml oil) during the oxidation of a white oil did not affect the oxidation rate, as measured by the change in dipole moment. However, with substantially more copper present (in amounts from 100 to 300 g/250 ml oil), there was some evidence of a slower rise in dipole moment after the withdrawal of the copper. But in these experiments the amounts of copper present were so enormous as judged by normal standards that it is possible that equilibrium in the dissolution-precipitation reactions had not been reached. Moreover, the dipole moment method of following the oxidation rate is unfortunately an indirect one, and at the copper concentrations present it seems likely that the dipole moment measurements may have been simply following, to a large extent, the net rate of dissolution of copper from the catalyst and its subsequent precipitation. Hence, taken in the light of our present findings, Kreulen's experiments cannot be regarded as conclusive evidence for the existence of a heterogeneous effect. It is possible, however, to visualize a situation where a " pseudo-heterogeneous " element of catalysis could exist. In such a case exceptionally high surface areas of copper would need to be present, and these might be sufficient to lead to such a rapid rate of copper dissolution that the precipitation mechanism could be completely overshadowed. (We have already shown in the sixth series of experiments that precipitation is not instantaneous.) A high oxidation rate might then persist for a short time after removal of the copper until sufficient precipitation of copper had occurred to reduce the soluble copper concentration to the level commonly found in that oil under normal oxidation test

Z

conditions. Such a type of behaviour, even if it were possible, is not, however, a cause for concern, for it could presumably occur only at copper concentrations far in excess of those normally encountered in practical oxidation tests.

DISCUSSION

The evidence accumulated during the course of the present studies has shown that under the conditions used, and with the oils investigated (a wide range in both cases), there is no significant contribution by a heterogeneous mechanism in the catalysis of oil oxidation by metallic copper. Moreover, the so-called variable corrosivity effect, although it has been shown to exist, is of no importance and it can be ignored, because it is completely overshadowed by the copper-precipitation reaction. This occurs so extensively under both metal- and soluble-catalysed test conditions as to cause the two sets of results to fall into a broad pattern of alignment.

With these conclusions in mind, it was considered expedient to examine the nature of the correlation that should therefore be expected to exist between metallic- and soluble-catalysed oxidation test results for the widest possible variety of oils. Results of this kind have become available during the course of investigations by ERA Panel E/Ab (see Gossling [9]), and also additional data have been obtained in the author's own laboratory on a range of commercially available transformer oils obtained from European sources. The results * are plotted in Fig 10, which illustrates how the expected correlation holds over three powers of ten for both sludge and acidity results. These results fit a single correlation line, which has a slope of very nearly unity, with apparently a small intercept on the soluble catalyst results axis. For convenience, both sludge and acidity results are plotted on the same numerical (logarithmic) scale. All the available data have been plotted for what may be termed "corresponding test conditions," *i.e.* conditions of time, temperature, and catalysis which result in approximately the same extents of oxidation. The corresponding conditions are as follows:

(1) 164 hours, 100° C, solid copper catalyst (IEC standard area, 9·73 sq. cm.).

(2) 164 hours, 110° C, 5 p.p.m. soluble copper catalyst.

(3) 48 hours, 110° C, 5 p.p.m. soluble copper plus 5 p.p.m. soluble iron catalysts.

From what limited evidence is available under other test conditions, it seems that the correlation line can be shifted, by a suitable choice of conditions, in the appropriate direction, remaining roughly parallel to the position shown in Fig 10. For example, "condition 2" oxidation, but for a shorter test duration, appears to result in a downward displacement of the correlation line, whilst a higher catalyst concentration (10 p.p.m. Cu), but retaining the original test duration, seems to cause an upward displacement of the line. In a similar way the 164 hours/100° C/10 p.p.m. soluble copper condition is very nearly a corresponding

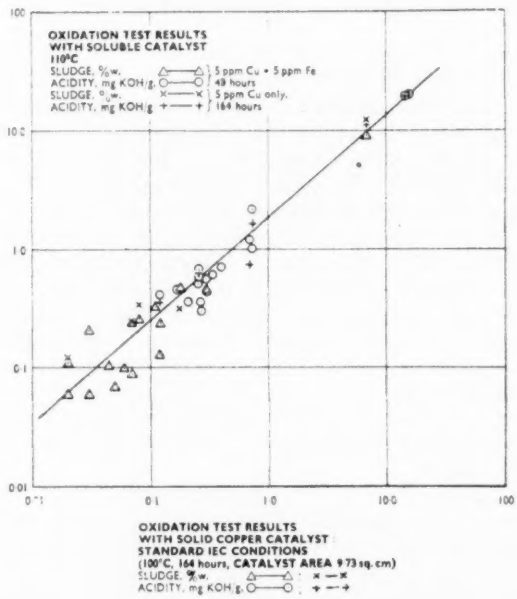

FIG 10

RELATION BETWEEN TEST RESULTS WITH SOLUBLE AND SOLID CATALYSTS

test condition, but in this case the soluble catalyst results fall just significantly below (and again, very nearly parallel to) the correlation plot of Fig 10 over its entire range. The points are not plotted, because the curve is not exactly coincident with the main plot, and would therefore tend to confuse the picture.

The existence of such a highly significant correlation between the test results with a metallic copper catalyst, on the one hand, and with a soluble catalyst, on the other, is regarded as sound confirmation of the conclusions expressed earlier in this paper that, in the catalysis of oil oxidation by metallic copper, there is no detectable contribution by a heterogeneous mechanism, and that the only important mechanism in the catalysis process is a homogeneous one.

There therefore remain no reasonable grounds to support arguments that oils could be mis-rated in oxidation stability by tests involving the use of suitably chosen concentrations of soluble catalysts. Overwhelming evidence has been presented both by

* Some of the points plotted represent the means of as many as 36 separate determinations.

Liander and Ericson,[7] and also in this paper, that no such suspicion can be attached to their use. The end-effect of catalysis by either metallic copper or a soluble copper salt involves only the soluble form of the metal, in a concentration governed more by the ability of the oil to retain the metal in solution than by the amount of metal or metal salt which is used in the test.

ACKNOWLEDGMENTS

The work reported in this paper was carried out in collaboration with other industrial laboratories as a contribution to the studies of ERA Panel E/Ad, "Oxidation Researches." The author wishes to express his thanks to V. Biske of Lobitos Oilfields Ltd, and P. W. L. Gossling of C. C. Wakefield and Co. Ltd, for the provision of some of the experimental results, and for their assistance in the interpretation of the information gained in this work. He is also indebted to his colleagues in the Control Laboratory, Thornton Research Centre, for experimental assistance; thanks are also due to the Electrical Research Association, and the directors of "Shell" Research Ltd, for permission to publish this paper.

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APPENDIX A

Determination of Copper in Sludges and Transformer Oils after IEC Oxidation Test

(Diquinolyl Method)

(1) *Scope*

This method describes a procedure for the determination of copper in the sludge and filtered oil from the IEC oxidation test.

(2) *Method Summary*

The oil is filtered on a glass sintered crucible and the filtered oil extracted with alcoholic hydrochloric acid. The copper in the extract is determined colorimetrically with 2:2′-diquinolyl.

The sludge collected on the glass sinter is oxidized with nitric and sulphuric acids, and the copper is determined colorimetrically in the solution obtained with 2:2′-diquinolyl.

(3) *Reagents*

(*a*) Diquinolyl solution. Dissolve 0·1 g 2:2′-diquinolyl in 100 ml industrial methylated spirit (I.M.S.).

(*b*) Alcoholic hydrochloric acid solution. Mix 10 ml conc hydrochloric acid with 90 ml I.M.S.

(*c*) Sodium acetate solution. Dissolve 30 g sodium acetate (anhydrous) in 100 ml water.

(*d*) Hydroxylamine hydrochloride solution. Dissolve 10 g hydroxylamine hydrochloride in 100 ml water.

(*e*) Standard solution of copper (A). Dissolve 1·0 g of pure copper in 30 ml of nitric acid (40 per cent), boil to remove nitrous fumes, and dilute to 1 litre (1 ml ≡ 0·001 g of copper).

(*f*) Copper solution (B). Dilute 10 ml of copper solution (A) to 100 ml with distilled water (1 ml ≡ 0·0001 g Cu).

(*g*) Copper solution (C). Dilute 10 ml of copper solution (A) to 1 litre with distilled water (1 ml ≡ 0·00001 g Cu).

(4) *Procedure*

Filtered Oil

(*a*) Weigh tube and oil and transfer contents (usually about 20 g) into a separating funnel. Add about 50 ml petroleum ether (40°–60°) and mix. Add 20 ml alcoholic hydrochloric acid, shake thoroughly for 2 minutes, and allow to stand 1 minute. Run off into a 100-ml beaker. Extract again with 10 ml alcoholic hydrochloric acid and transfer to beaker. Evaporate extracts carefully on a hot plate to dryness.

(*b*) Dissolve any residue left in original tube with 2 or 3 ml conc sulphuric acid and transfer to beaker. Add about 5 ml conc nitric acid to the tube, swirl to dissolve any remaining residue, and transfer contents to the beaker. Wash, dry, and weigh the tube and calculate total weight of oil.

(*c*) Heat gently and wet oxidize contents of beaker until solution is colourless. Evaporate to incipient dryness—volume of sulphuric acid should not exceed 0·5 ml. Cool, add 10 ml distilled water, and boil for 1 minute. Transfer to 100-ml separating funnel and wash in with 2 × 10 ml distilled water.

(*d*) To this solution (30 ml) containing not more than 0·5 ml conc sulphuric acid, add 10 ml sodium acetate solution (shake), followed by 10 ml hydroxylamine hydrochloride (shake), and then 5 ml diquinolyl solution. After each addition shake well. Extract purple colour formed by shaking with 10 ml chloroform for 2 minutes and allow to stand for 1 minute. Run off chloroform layer into 50-ml graduated flask containing 2 or 3 ml I.M.S. Extract with a further 5 ml chloroform, allow to stand for 1 minute, and transfer to flask. Make up to the mark with I.M.S. Filter if necessary and measure optical density at 546 mμ using ½-, 1-, 2-, or 4-cm cells.

(*e*) Extract the test solution again with 5 ml diquinolyl to make sure that all the copper has been extracted. Do a blank on all reagents.

Sludge

(*f*) Place the crucible containing the sludge in a 100-ml squat beaker with about 10 ml conc nitric acid. Fill the crucible with conc nitric acid and cover the beaker with a watch glass. Heat gently on a hot plate until all the residue is dissolved —add more nitric acid if necessary. Remove the crucible and carefully wash with distilled water. Add 2 or 3 ml of conc sulphuric acid to the beaker and evaporate contents to fumes of sulphur trioxide. Oxidize with nitric acid until solutions are colourless and evaporate to incipient dryness. The volume

of sulphuric acid at this stage should not exceed 0·5 ml. Add 10 ml of water and boil for 2 minutes. Cool and transfer to separating funnel (100 ml). Wash the beaker with 2 × 10 ml distilled water and transfer to separating funnel. The volume should be approximately 30 ml.

(*g*) Add 10 ml sodium acetate solution (shake), 10 ml hydroxylamine hydrochloride (shake), followed by 10 ml diquinolyl solution. After each addition shake well. Extract with 20 + 10 ml chloroform by shaking thoroughly for 2 minutes. Transfer chloroform layer into a 100-ml graduated flask containing 5 ml I.M.S. Dilute with I.M.S. and make up to mark.

(*h*) Add a further 10 ml diquinolyl to make sure that all copper has been extracted. If present, extract with chloroform, etc., and make up to 100 ml.

(*i*) Filter if necessary and measure optical density at 546 mμ using ½-, 1-, 2-, or 4-cm cells. Do a blank on all reagents.

(5) *Calibration*

The calibration is carried out exactly as in 4 (*d*) on known amounts of Cu in the ranges as follows:

For Cu in the range 0 to 0·1 mg use 4-cm cells.
For Cu in the range 0·1 to 0·2 mg use 2-cm cells.
For Cu in the range 0·2 to 0·4 mg use 1-cm cell.
For Cu in the range 0·4 to 0·8 mg use 0·5-cm cell.

Pipette amounts of standard Cu solution, in the range required, into a separating funnel and determine Cu as in 4 (*d*). Carry out a blank. Determine optical density at 546 mμ. Correct for blank and draw calibration curve for cells required.

(6) *Calculation*

Refer the optical density of the blank and sample experiment to the calibration graph. Report Cu content of oil as p.p.m. and copper content of the sludge as a percentage, or as p.p.m. of the original oil weight before IEC oxidation.

APPENDIX B

Analytical Characteristics of Insulating Oils

Insulating Ref. Oil	1	2	3	4	5	6	GB II	Spec. Limits
Sp. gr. at 60/60° F	0·877	0·885	0·867	0·869	0·878	0·867	0·881	
Flash point (P–M), closed cup, ° F	320	290	300	310	300	315	310	
Viscosity kinematic at 100° F	15·1	16·0	14·3	14·7	14·7	14·6		
Kinematic viscosity index	37	36	55	45	45	46		
Pour point, ° F	−50	−50	−50	−50	−35	−50	−45	
Iodine value (Wijs)	9·6	13·1	0·9	2·1	7·4	1·1		
Refractive index, N_D^{20}	1·4798	1·4864	1·4729	1·4746	1·4810	1·4733	1·4830	
Aromatic content, % wt *	19·3	27·0	5·6	9·8	17·9	5·9	20·0	
n–d–M type analysis:								
Aromaticity	3·2	11·0	1·0	2·0	7·0	1·0	9·0	
Naphthenicity	43·6	39·5	45·0	45·0	42·0	45·1	38·1	
Paraffinicity	53·2	49·5	54·0	53·0	51·0	53·9	52·9	
P/N ratio	1·22	1·25	1·20	1·18	1·21	1·20	1·39	
British (B.S. 148) oxidation test:								
Sludge value, % wt †	1·27	1·36	0·63	1·18	0·93	0·66	0·75	1·2
Acidity after oxidation, mg KOH/g †	1·81	1·73	4·53	2·94	1·50	4·07	1·30	2·5
Swiss (SEV) oxidation test:								
Sludge 3 days	0·07	0·01	0·01	0·04	0·02	<0·01		—
Sludge 7 days	0·23	0·08	0·11	0·08	0·05	0·07		0·15
Acidity 3 days	0·28	0·18	0·60	0·25	0·03	0·55		0·30
Acidity 7 days	0·50	0·22	1·45	0·40	0·14	1·60		0·40
Decrease in tensile strength of cotton thread, %:								
3 days	8 increase	1	39	5	2	54		25
7 days	5	20	65	37	10	67		35
German (V.D.E.) oxidation test:								
Appearance of oil after test	Clear	Clear	Solid matter present	Clear	Clear	Solid matter present		Clear
Sludge	Nil	Nil	Present	Nil	Nil	Present		Nil
Tar No.	0·24	0·08	5·5	0·08	0·05	6·8		0·1

* Obtained using the method described by G. H. Beaven, L. F. Foster, and C. N. Thompson, *J. Inst. Petrol.*, 1950, **36**, 314.
† Average of results from two laboratories. The sludge values for I.R.O. 1–6 were obtained at a time when the specification limit was 1·1 % wt, *i.e.* prior to Nov. 1956, when *n*-heptane was introduced as a precipitant in the B.S. 148 oxidation test.

DISCUSSION

P. W. L. Gossling: We are especially fortunate in having with us Sir Harry Melville, F.R.S., who has kindly agreed to open the discussion. It is relevant that, as a member of the Electricity Research Council, Sir Harry should speak upon our subject, but particularly so because, at an earlier stage of the ERA-sponsored work at universities, we had the benefit of his advice in planning the work to be carried out in the Department of Physical Chemistry at Birmingham. We are very pleased that, with his greatly increased responsibilities as Secretary to the Privy Council for Scientific and Industrial Research, he is still able to give time to talk to us to-day.

Sir Harry Melville, F.R.S.: Professor Morton has already emphasized that everyone is in agreement about

the main steps of the oxidation reaction once it has got going, and he and Professor Robb also emphasized that the rate determining step in that reaction was the dehydrogenation of the hydrocarbon by the RO_2 radical. This state of affairs holds good, provided that the oxygen concentration in the system is reasonably high. But it is quite possible that under practical conditions, especially in transformers, the oxygen concentration might fall to much lower values, in which case, instead of the rate determining step in the oxidation reaction being the dehydrogenation of the hydrocarbon by the RO_2 radical, the rate determining step might be in fact the addition of the oxygen molecule to the radical R representative of the hydrocarbon. If that happens, it means that the concentration of the radicals, R, will tend to rise relative to the RO_2 radicals, and correspondingly, the termination of the oxidation may then occur, either by the interaction of the R radical with the RO_2 radical, or even, under extreme conditions, by the interaction of the two R radicals. If that happens, maybe the mechanism of the termination process, by inhibitors, could be significantly altered, because that termination reaction, instead of involving the interaction of the RO_2 radical with the inhibitor, might involve the interaction of the R radical with the inhibitor.

That is just one point. The second is the much more difficult problem that in most of these systems one is dealing, not with a pure hydrocarbon, but with a mixture of hydrocarbons, and these hydrocarbons will simultaneously undergo oxidation. Professor Morton did show on a slide the considerable anomalies that appear when one deals with a multicomponent system. In oxidation mechanisms it has been possible hitherto to deal with the two-component system and to work out all the various steps that occur. When it comes to a multicomponent system the problem is very much more complicated, but fortunately there are methods whereby it might be tackled. The same problem arose some years ago when dealing with the kinetics of the polymerization system where radicals are involved, and it proved possible then not only to tackle completely the elucidation of the mechanism of the polymerization of the two-component system, but also, in fact, to deal with a three-component system, where the number of elementary steps involved may rise to twenty, at least. The trouble is that the analytical and even the mathematical techniques needed for the analysis of the results are very complicated. But the principles of the method of approach have been laid down, and therefore it might be possible, after further experiments have been made, to tackle the problem of co-oxidation in a multicomponent system. It would not be easy, but it might help to solve some of these anomalies which Professor Morton mentioned in his paper.

The next point is the precise mechanism of the termination of these reaction chains. Again, it has been established kinetically that the rate-determining reaction there is the interaction of the RO_2 radical with the added inhibitor, usually involving the dehydrogenation of the inhibitor molecule. Of course, if that happened, it means that although the RO_2 radical now becomes stabilized by its acquiring a hydrogen atom, there still remains within the system a free radical derived from the inhibitor. The question is: what part does that radical play? Kinetically it is usually convenient just to forget all about it and to assume that it disappears by a mechanism which does not affect the kinetics of the oxidation.

Again, I would like to draw an analogy with the similar state of affairs in polymerization, where it has been shown recently in a number of papers that if one neglects the fate of the radical derived from the inhibitor, then one can sometimes get into very serious complications. I just wonder in these oxidation reactions whether again it is necessary to be a little more careful about the description of some of the kinetics of these reactions, especially when they are retarded or inhibited, and to take into account what happens to these residual radicals.

That is also bound up by another problem, which is a very difficult one in this particular case. One can analyse the kinetics and write down an acceptable scheme which everyone agrees about, but that does not necessarily mean that we know anything about the precise chemistry of the reactions of these RO_2 radicals with the inhibitors. If one could devise ways and means, *e.g.* by using radioactive tracers as inhibitor molecules, of finding out something about the chemistry of these interactions, and particularly the chemistry of the fate of these radicals derived from inhibitors, then again some of the anomalies which always crop up in these reactions might be more clearly resolved.

There is just one other point which always worries me about oxidation reactions, particularly when inhibitors are present, and that is that one normally assumes, in dealing with retarded and inhibited reactions, that only one of the radicals involved in the propagation of the chain interacts with the inhibitor molecule. But as has been seen already, from Professor Bawn's discussion, there may be other radicals produced in the initiation process which will react with the inhibitor. That means that the chemistry of the process is quite different from the interaction of the RO_2 radical with the inhibitor, and therefore such a reaction has to be taken into account. It is not very easy to identify the products of such a reaction; that is certainly a problem for the future. These are some of the matters which are bound to need consideration in the near future, because the techniques for investigating the kinetics in more detail, and the analytical techniques for finding out what is produced in these reactions, are becoming more refined. I think there is a good chance in the not-so-distant future that some of these anomalies may be properly resolved.

Professor H. Weiss: We have heard about some fundamental work on oxidation mechanisms, and we are convinced that this new knowledge will be of great help when the decision is taken concerning the design of the International Test Method.

I would like to emphasize the fact that we know that the technical phenomena of oxidation are certainly not unique; we must abandon the idea of choosing one mechanism which would be the only one and the best one. I would like to remind you of the work by Vellinger and Muller (1938), which does not seem very widely known. This shows that if one takes a crude distillate and refines it more and more, one can represent the results obtained by a graph showing oxidizability *v.* degree of refining, *i.e.* the amount of oxygen absorbed during aging as a function of amount of sulphuric acid used. When the degree of refining is increased, one sees first the oxidizability diminishing slowly and afterwards suddenly greatly increasing. The oil components are almost the same (*i.e.* there is only a very slight change in the bulk constitution of the oil), but the oxidation mechanism changes completely. With heavily-refined oils, one gets significant amounts of water, CO_2, and volatile oxidation products; the sludge, when present, is red and resinous. With lightly-refined oils, there is almost no formation of water and CO_2; the sludge is dark and powdery. So there are at least two oxidation mechanisms of technical interest. The best-refined oils are situated near the junction of the two oxidation mechanisms; on the right-hand side of the graph a bigger amount of volatile matter is formed as oxidation pro-

ceeds. This has great importance for the artificial aging test.

We have heard that copper is not a good catalyst, but it is our catalyst, because when in Stresa (1949) we had to design a scheme for the International Artificial Aging Test, we chose a procedure which would allow us to benefit by all the practical experience which had been gathered, from Europe and elsewhere, during the past twenty years.

This experience has been based on the use of a copper catalyst; as Mr Gossling explained, there is always copper in the transformer and in the oil.

H. Liander: Professor Morton and Dr Bell present a very interesting theory on the function of copper as a catalyst in the oxidation of oils. Peroxides are formed in the oil, break down at the copper surface, and bring the metal into solution. The copper ions thus formed catalyse the further oxidation of the oil, and the copper is precipitated with the oxidation products. If the supply of oxygen is limited, as would be the case in a transformer, where the oxygen is carried to the copper by diffusion, it is momentarily consumed near the copper surface, with the consequence that there is a continuous sequence of oxidation periods.

This would not be the case in an accelerated test where air or oxygen is blown through the oil.

One might thus be tempted to draw the conclusion that in evaluating the oxidation characteristics of transformer oils it would in principle be wrong to use such accelerated tests. This would indeed be regrettable. Not only would we be deprived of a valuable means of acceleration, but comparable tests within the IEC have shown that the reproducibility of tests with oxygen diffusion is very poor.

Fortunately there is in my opinion an overwhelming amount of evidence that tests with oxygen bubbling through the oil will rate the oils in the same order as their actual performance.

From a theoretical point of view it might be possible that some catalysis is effected by solid copper, as Morton and Bell say. But I agree with Mr Thompson that it can be of no practical importance. It has been shown by ourselves, and also by the British investigations reported at this symposium, that without exception aged oils contain copper in solution. Moreover, the sludge deposited in transformers also contains appreciable amounts of copper. We have found from 0·1 to 2 per cent.

I should also like to stress that in examining samples of used transformer oils by an accelerated oxidation test according to the IEC method, but without further addition of metal catalysts, we have found that the oils behave in a way to be expected from their original contents of copper and iron in solution.

Professor Weiss favours one catalyst, *i.e.* copper. I have two favourites, copper and iron. As I see it there is a tendency to underrate the influence of iron in the oxidation of transformer oil. It appears that iron does not dissolve so readily in the oil as copper, but once dissolved remains in solution longer. In nearly all the used oils we have analysed, and in most of the cases reported by Mr Gossling, the iron content is higher than the copper content. It is significant that the case is reversed in sludge collected in transformers.

I am much impressed by the careful investigation reported by Mr Thompson. He has certainly filled a gap in our knowledge of the role played by copper in the oxidation of oils. As pointed out in his report, my co-worker Mr Ericson and I have shown that variations in the rate of dissolution of copper in different oils had little influence on the subsequent oxidation rate of the oils. Or to be more clear; comparing solid and dissolved catalysts we found no difference in the rating attributable to the variations in corrosivity.

We produced no explanation and find it very gratifying that this has been done in such a convincing way by Mr Thompson.

I fully share the opinion expressed by Mr Gossling in his excellent résumé that the result so far obtained by the IEC Technical Committee No. 10 does not satisfy the requirements set at the Stresa meeting. I am afraid, though, that we could not have come so far if it had not been for the British efforts. I hope that these will lead to a modification of the IEC method.

Dr T. Salomon: The results presented in the different papers show very clearly that there are many ways to oxidize oil, but the results obtained are not necessarily identical. We worked on similar lines for more than 30 years and came to the conclusion that the important thing is not to know how the oil is oxidized, but why it is oxidized. Starting from this point of view, one may find that oxidation as a chain reaction needs the presence of an initiator. Such an initiator will act even when it is present in the oil in very minute concentration, of the order of 10^{-6} mol or less, and it is strange that this effect of traces has not always been clearly recognized. The initiator may exist in the oil before oxidation, or may be introduced into the oil when adding a soluble catalyst, such as peroxide, aldehyde, metallic soap, and so on. But when the oil is refined to such an extent that the last traces of all these initiators have been eliminated, no oxidation will occur, even at high temperatures and in the presence of metallic catalyst. When the purified oil is contaminated with a trace of an initiator, oxidation of the oil will become possible. Working on these lines, it has been possible to prepare completely purified oils which could no longer be oxidized, not only hydrocarbon materials, but also synthetic products hitherto considered, according to their chemical constitution, as low-stability compounds. The chemical nature of some of these initiators of the oil oxidation is known, but not that of all "starters," and this field is still wide open for further research.

Whereas a purified oil cannot be oxidized, a contaminated oil will be oxidized, but only to a limited extent. This limit may vary with the nature of the contaminant, for a given oil, but it never exceeds, say, 10 to 20 per cent of the oil tested. It has never been possible completely to oxidize an oil; contamination of an oil in operation by insufficiently polymerized varnish is an illustration of this. Hence the oxidation is stopped as soon as the initiator present is consumed by side reactions. The effect of the initiator on a given oil depends on the presence of reactive compounds in the oil, which will react with the initiator. We understand now why the same initiator may have a different effect on different oils, and why the results obtained may vary with the test conditions, such as temperature, oxygen availability, etc.

The catalyst added to such a contaminated oil may be without effect, and this is shown by Mr Thompson for I.R.O. oils No. 3 and No. 6, for instance, which are already contaminated, so that the addition of catalysts has no marked effect on acidity formation (see Table III). From the practical point of view we have to consider two types of contaminants, those normally encountered in refined oils, which cannot easily be removed, and those incidentally encountered in refined oils, which have to be removed, such as traces of metal soaps, active sulphur compounds, etc. An aging test has to take account of the first type of contaminant and must show that its

effect on the oil's stability is limited; the test must not be based on results obtained with incidentally-contaminated oils; these oils must be *ipso facto* eliminated by the test. We know, for instance, that oils containing metal soaps are not suitable as insulating or turbine oils, as they have low stability, so we would not use such low-stability oils to work out the basic principles of an aging test. From this point of view, it may perhaps be a drawback that the majority of the oils tested by Mr Thompson are " contaminated " oils, as the conclusions drawn are based on results which may be open to criticism.

As has been clearly stated by Mr Gossling, an oil contaminated by varnish products will undergo more rapid

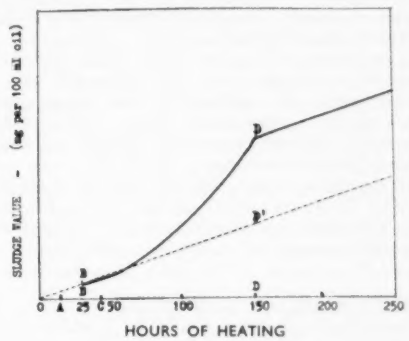


FIG A

SCHEMA OF THE DIFFERENT PHASES IN THE ARTIFICIAL AGING OF A MINERAL OIL WITH SOLID COPPER

OA—preliminary phase where copper has no action
AC—zone of action of the solid copper catalyser
B—starting point of sludge formation
BD—normal sludge curve with auto-catalytic acceleration
BD′—sludge curve without auto-catalytic acceleration
D—normal sludge value found with copper present during the whole time OD or during the period corresponding to OC or AC (case of aging with auto-catalytic acceleration)
D′—sludge value found when the action of copper is limited to the period OB or AB (case of aging without auto-catalytic acceleration)

oxidation; it should not be concluded from such a result that the oil has a low stability, but that the oil is contaminated. When working out an aging test we have to work with " normal " oils and thereafter to verify that the contaminated oils will fail the test owing to the contamination present; otherwise a conclusion may be reached which is not confirmed by practice.

Now we come to the problem of solubilization of copper by the oils, to which much work has been devoted. In this connexion, we must keep in mind three well-established facts. Solid copper, as already pointed out by Professor Bawn, is not an oxidation catalyst. Solid copper acts only during the inhibition period as a dehydrogenation catalyst, in favouring the formation of free radicals by the dehydrogenation of some molecules. As the action of copper is limited to the initial phase of the oxidation, copper may then be taken out without reducing the speed of the oil's oxidation. We have demonstrated this fact in a paper presented in 1931 to the Zurich Congress of the International Association for Testing Materials,* see Fig A, and Mr Thompson's results confirm this conclusion. Solid copper does not participate at all in the oxidation of a normal oil, and this is shown by the results of Mr Wood-Mallock and his colleagues, who state that there is no correlation between the content of copper dissolved in the oils and the acidity development during the aging test.

The thermal effect produced on an oil lowers its chemical stability, not the copper dissolved during the pre-heating of the oil, as admitted by Mr Wood-Mallock (Table III). It was shown in our paper to the ASTM Symposium in 1954 † that prolonged pre-heating at low temperature, 50° to 60° C, without copper, is quite sufficient to lower the stability of an oil. One of the aims of oil refining is to eliminate the thermally unstable compounds from the oil. This clearly explains the better results obtained by Mr Wood-Mallock when intensifying the refining of the oils.

How, then, are we to explain the presence of small quantities of copper in the oils? We agree with Mr Wood-Mallock that traces of acidic compounds promote the solubility of copper. However, by acidic compounds we do not mean carboxylic compounds, but aldehydic compounds. How can we explain the presence of minute traces of dissolved copper in oils which do not contain aldehydic compounds, traces as high as 10^{-7} according to the figures given by Mr Thompson, Mr Wood-Mallock, and his colleagues? These small quantities of copper may not exist as a soluble copper compound, as in the case of the presence of an aldehyde, but as small metal particles peptized by the oil. The solid metal used as a catalyst, even carefully cleaned, may retain very fine submicroscopic particles on its surface which are eliminated by the rubbing effect of the oil in motion during oxidation and maintained in the oil in a peptized state. This means that we have to deal with a " wash " effect

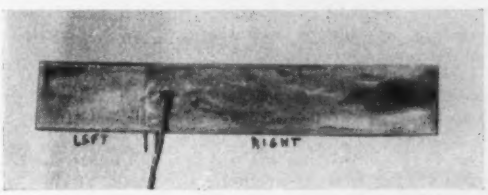


FIG B

" WASH " EFFECT OF MINERAL OIL ON COPPER DURING OXIDATION

(*Left*) Copper cleaned only mechanically
(*Right*) Copper cleaned electrolytically

of the oil and not with a solution effect. This " wash " effect will be more marked when the copper is electrolytically cleaned, as the metal surface will retain more particles loosely attached and more easily removed by " washing." This is clearly shown in Fig B, which shows the appearance of a small copper plate after several hours immersion in a mineral oil maintained at 115° C in an open vessel. The left side of the plate was only mechanically cleaned, while the right side was been cleaned both mechanically and electrolytically. The " wash " effect is more marked on the right side of the plate.

* International Association for Testing Materials. Zurich Congress (September 1931), Vol. II, p 256.

† Salomon, T. " The Performance Characteristics of Used Insulating Oils." ASTM Symposium (Evaluation of Insulating Oils—European Developments), Cleveland, Nov. 1954: ASTM Special Technical Publication No. 172, 1956, pp. 24–47 (see Fig 3, p. 27)

The figures given by Mr Thompson, Mr Wood-Mallock, and his colleagues show quite clearly that these minute amounts of metallic copper peptized by the oil have no significant effect on the oil stability.

The statement by Mr Thompson that oil sludge, even when containing copper, has no catalytic effect on the oil oxidation, confirms our findings during our study of the mechanism of the aging of oils in service in transformers, which we started in 1926. We added 125 p.p.m. of transformer sludge to five new oils of different chemical stability before putting them into service. Observations made annually during a period of thirteen years showed no difference in the performance of the contaminated and uncontaminated oils. The results have been published by E. Pellissier in the CIGRE Reports from 1927 to 1939.

The static absorption of Mr Massey and Mr Wilson uses oxygen produced by electrolysis. May I recall the work done by Professor Perrottet of Geneva in 1937,* who studied the oxidation of benzaldehyde and established that the speed of oxidation varied with the ozone content in the air used as oxidant. The ozone content is much higher in oxygen prepared by electrolysis than in that obtained from liquid air. For this reason it is preferable to use Linde-oxygen, as specified for the IEC test. The influence of traces of ozone present in the oxygen used on the mechanism of the oil oxidation has not yet been fully recognized.

J. C. Wood-Mallock: Twelve years does not seem very long by normal standards, but when employed on research it is quite a time, and I think that these twelve years since 1946 have taken us a big step forward.

Twelve years ago the problem was, by and large, " Is the oil good enough? " We were examining methods of test, but we were equally concerned with difficulties being experienced in operation. My own particular problems were those of the refiner rather than the user. One of these problems was that some ten or twelve years previously we had experienced rapid deterioration of insulating oils during manufacture, and immediately afterwards we found that some of the deterioration could be attributed to the presence of traces of metals. The traces, very small quantities indeed, of the order of from 0·5 to 5 p.p.m., derived from our refining methods and the materials of plant construction.

Our work at the time enabled us to eliminate the trace metals arising from the refining processes, but we then came up against the further deterioration which took place on storage. It was apparent that the oil contained compounds which attacked the ordinary materials of construction, in particular, copper and iron, and we tried to improve it in this respect. We were quite unsuccessful at that time, but in 1946 the previous symposium was held and general attention began to be focused on metal catalysis both from the analytical and practical viewpoints.

This symposium has shown that that attention was well deserved. We have had a definitive paper from Mr Thompson which is going to affect the methods of test used internationally. He has shown that an oil has natural characteristics which control its response to soluble copper. My colleagues and I have some ideas on how to modify this natural response and in fact to neutralize it, and I think that both these developments are of first importance.

The question then arises as to what use will the practical man not directly concerned with research or theoretical developments make of this knowledge. Mr Thompson's work will influence testing methods and thus lead to better oils. Ours will make the better oils last longer or stand up to more severe operating conditions. It may be, however, that we are still not going about this problem in the right way. After all, the whole trouble stems from oxygen, and it is not really such a terrific job to limit oxygen access to the oil in the transformer case. Perhaps during the next ten years we can be giving some thought to this problem which, if solved, would put an end once and for all to this comparatively, to the electrical engineer, minor problem of transformer oil deterioration.

W. N. Clinch: I feel that it would be inappropriate if the references which have been made to the ERA were not acknowledged on this occasion. I think the efforts of the co-operative research have made it possible for this session to be held, and I think I would like to use, in this regard, the references that were made by Mr Thompson. I would have to say, but I would use the words in a different meaning, that the heterogeneous discussions which have been held have made a homogeneous response possible this afternoon. I am a member of the ERA, and am chairman of the Finance and General Purposes Committee, and I am obliged that the prestige of that association has been established again.

C. N. Thompson: It is gratifying to hear the kind remarks made in the discussion by Mr Liander, Mr Wood-Mallock, and others about the contribution made by the industrial group of laboratories of ERA Panel E/Ad. We believe our findings have added something to existing basic knowledge about the mechanism of catalysis by metals, and metal scraps, in oil oxidation. It is our hope that this new knowledge will help to speed up the acceptance, internationally, of a quick, simple, and reliable test method for assessing the oxidation stability of insulating oils. The work of the industrial group can be considered as exactly complementary to the more fundamental approach of the three British universities represented on ERA Panel E/Ad. The cross-stimulus of ideas and thoughts from the academic and industrial research people has been a most valuable feature in our investigations.

Some people have perhaps felt that progress in this direction during the last ten years has been a little lethargic. But we must not confuse lethargy with caution. It is vital, in a venture of this kind—with its international implications—that we base a new and universal test on a sure footing. This, in turn, means that we must be certain of our facts before making positive recommendations for adoption by the various national bodies. It has been our aim in the studies that we have made in Great Britain to ensure that we learnt the truth—and the whole truth—about catalysis mechanisms.

Professor Weiss and Mr Liander both said a few words about the sort of catalyst needed in an oxidation test. I am wholeheartedly in agreement with Mr Liander that we should not forget iron, which is an important constructional material of transformers. In the metallic form, iron does not seem to be so powerful a catalyst as copper. But in the soluble form, it is just about as active. I say " just about " because it is possible that some oils may respond more than others to a few p.p.m. of soluble iron.

Of all the data accumulated in the course of our in-

* Briner, E., and Perrottet, E. *Helv. Chim. Acta*, 1937, **20**, 293.

vestigations in Great Britain, we probably have the largest amount from IEC-type tests using 5 p.p.m. soluble copper plus 5 p.p.m. soluble iron. This would seem to be a happy catalyst combination, because, in as little as 48 hours at 110° C one obtains results correlating very well indeed with those of metallic-copper-catalysed tests running for 164 hours at 100° C or 48 hours at 110° C. Moreover, there is strong statistical evidence that the precision of oxidation test results obtained with this soluble catalyst combination is much better than the precision with the metallic copper catalyst.

We are not perhaps yet at the stage when we can say that this is the " right " (or even the best) combination of catalysts and test conditions. In fact, there is probably no such thing as the " right " set of conditions which will always correlate perfectly with what happens in service. We know that changes in catalyst concentration, catalyst surface area, and perhaps variables such as oxygen-diffusion and temperature may cause changes in the merit-ratings of groups of oils. In all probability, this applies equally in the laboratory and in service.

However, the evidence leads us to suppose, at the present time, that there is not much wrong with 5 p.p.m. Cu + 5 p.p.m. Fe/48 hours/110° C for giving a good all-round indication of the oxidation stabilities of insulating oils of widely differing types. No doubt, with a little more investigational work, and a more detailed analysis of the data (only some of which is reported in the papers by Mr Gossling and by myself), we shall be able to take a further step forward in this matter of international standardization.

I found it rather difficult to understand some of Dr Salomon's remarks, particularly those where he says that a really purified oil (*i.e.* contaminant-free) cannot be oxidized, even at high temperatures. Along with Mr Biske, I would dispute this contention. We all know that highly-refined oils, even those prepared in the laboratory by the most modern separative methods to ensure freedom from contaminants and initiators, are most prone to oxidation. The same applies to pure hydrocarbons, some of which can be very highly purified, but which peroxidize very readily even at low temperatures, *e.g.* tetralin in storage in the laboratory.

Dr Salomon mentions that catalysts added to contaminated oils may be without effect, and cites as examples I.R.O. 3 and 6. This is not quite true, because there is, in fact, a significant effect on the sludge value—if not on the acidity—as one increases the catalyst area. The data are in Table II of my paper.

Dr Salomon goes on to say that it may perhaps be a drawback that the majority of the oils used in our British investigations are " contaminated " oils, and that the conclusions drawn are based on results which may be open to criticism. This looks a serious allegation on the face of it, but fortunately I can assure Dr Salomon that we can dispose of it very easily!

If one looks at Table III of my paper, one finds results for the distribution of " dissolved " copper between the oil and the sludge, and figures for the total amount of copper that dissolved from the metallic catalyst as we increased the surface area. I am afraid that Dr Salomon is reading too much into the figures quoted for the tests that we did with no added catalyst.

In every case but one we found a tiny amount of copper in the oil, the sludge, or both, even though we had not used any copper catalyst at all in the test. However, except in two (I.R.O. 3 and 6) out of the seven oils examined without catalyst, the totals (*i.e.* soluble copper remaining dissolved in the oil, plus that precipitated in the sludge) were not very different from the experimental accuracy that we claim for our method of analysis (0·5 p.p.m. or better). In other words, we are working at or near the limit of sensitivity of our analytical method, so it is not justifiable to say that the oils are contaminated.

Dr Salomon will be amused to learn that at first these results puzzled us, as they did him. So we took the precaution of checking the copper contents of the oils directly, instead of relying on the figures quoted in the table, which relate to oils that have been oxidized in the IEC test, and worked up in the usual way with *n*-heptane, and filtration, to give the sludge and so forth. The " direct " figures we obtained on the oils before oxidation were in all cases smaller than (or in one case the same as) the " indirect " totals for the oxidized oils and sludge. We took this to mean that, during oxidation and subsequent working up, the oils had picked up a small extra amount of copper, perhaps from the oxygen stream, from the glass-ware, the sintered filters, or even the laboratory atmosphere. We all know that soluble salts are, in fact, very readily adsorbed on glass, and even despite the precautions that we took, the oils might have picked up some slight additional " contamination."

It is evident that the " contamination "—even if it is real—can be neglected in considering the results obtained, which with increasing areas of metal show very regular and definite trends. It is perhaps significant that the oils with the least " contamination " are the most stable over the entire range of catalyst conditions; those with the higher amounts are the least stable. The instability may be the reason why they picked up the contamination, and not vice versa, as proposed by Dr Salomon.

Dr Salomon's theory of mechanical removal and peptization of metallic particles is an interesting one, but I should like to see more evidence for it. There may be other reasons for the differences between abrasively—and electrolytically—cleaned copper surfaces.

CONTRIBUTED DISCUSSION

Professor H. Weiss: I found it rather difficult to reconcile exactly what is said in C. N. Thompson's paper and some of the remarks that he made at the symposium in covering the highlights of the work done by the British group of industrial laboratories represented on ERA Panel E/Ad. In presenting his paper Mr Thompson said the following:

> " Using the IEC oxidation test with a wide range of catalyst conditions and oil types, we showed clearly that oils vary in the extents to which they dissolve copper. This was not new information. It was already known but it is one of the reasons why some people used to dislike soluble catalysts. They felt that the use of a soluble catalyst in a fixed concentration might penalize unfairly those oils which were relatively non-corrosive towards a metallic copper catalyst. This is not so and I will tell you why in a moment. We then went a stage further and showed something much more important. This was

that oils vary much more in their ability to precipitate copper from the dissolved form into an inactive form in the sludge. The extent and rate of oxidation depends not only on the amount of copper dissolved from the catalyst but on the amount which does not precipitate from the dissolved form.

"The curious feature is that exactly the same thing happens when one uses a soluble catalyst from the start. Most of it precipitates into a catalytically-inactive form, as can be seen from the figure:

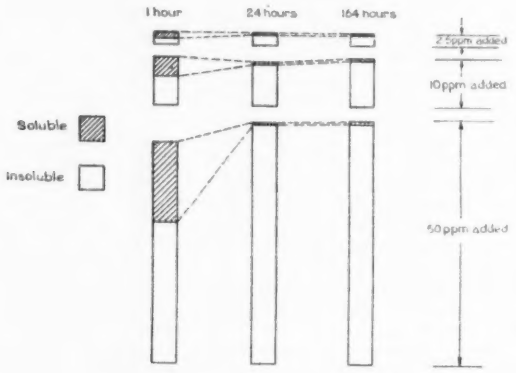


FIG C

SOLUBLE COPPER CATALYSIS: COPPER REMAINING DISSOLVED AND BECOMING PRECIPITATED

(Averages over all oils)

The copper that is left in the soluble form is what governs the rate of oxidation. As will be seen, the set of results quoted on the left refers to one hour test duration, the middle set to one day, and the right hand set to about one week. We have not quite reached equilibrium in one hour results but we do so very shortly afterwards.

"Apart from the results in the first hour, the copper remaining soluble is not so much a function of time, or of the amount or type of catalyst that we start with. It is, however, very specific to the oil that we are testing.

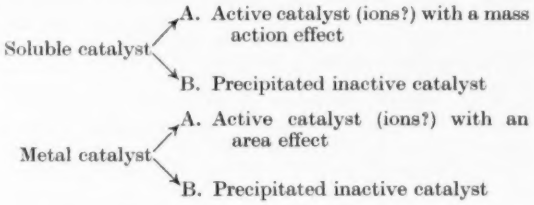
"Furthermore, we have shown that the removal of metallic copper catalyst from an oxidizing oil at an intermediate point in the IEC test has absolutely no effect on the rate or extent of the subsequent oxidation. There is no discontinuity whatever in the oxidation rate curve. This means that the copper surface itself has no separate catalytic effect other than that of providing soluble copper to act as a single-phase catalyst. In other words, there is no contribution by a heterogeneous mechanism."

The points that I should like to make are as follows:

(1) If all excess copper is precipitated it is necessary to explain why there is an absence of an effect of different concentrations of soluble catalysts but the existence of an effect with different areas of solid copper.

(2) There should be with solid copper a replenishing effect upon the copper in solution, so that the differences in conductivity should be important.

(3) It seems possible that one might compare the mechanisms of catalysis by the two kinds of catalysts in the following way:


Soluble catalyst
A. Active catalyst (ions?) with a mass action effect
B. Precipitated inactive catalyst
Metal catalyst
A. Active catalyst (ions?) with an area effect
B. Precipitated inactive catalyst

The distribution as between mechanisms A and B would vary with different oils. In other words, if a catalyst is introduced in a dissolved form there would need to be an intermediate reaction before it passes into the active form. However, such a reaction would be a homogeneous one, whilst dissolution of metallic copper is a heterogeneous reaction. More work would be required in order to amplify this aspect but I think, from a practical point of view, Mr Thompson's paper gives us the data we require.

(4) I think the greatest help which Mr Thompson could give would be to put forward, based on the data in his paper, suggestions concerning, on the one hand, the most suitable concentration of soluble catalyst, and on the other hand, the most suitable copper wire area which would in either case give the most rapid oxidation rates, and which would class the different oils examined in the same order. If he could put forward clearly such a conclusion, then he would render considerable help towards our common objective, which is to devise a quick and reliable international oxidation test.

C. N. Thompson: In reply to Professor Weiss' first point, this probably arises because, in presenting my paper, I probably over-condensed and over-simplified the point at issue. If one compares, on the one hand, Fig 1 and Fig 2, with Fig 8 and Fig 9, on the other hand, one will find that with both kinds of catalyst (metallic and soluble) there are comparable effects on acidity and sludge when one increases the area and concentration respectively. These effects are, in my opinion, due to the time factor. By this I mean that at the larger areas of concentrations, the overshadowing precipitation effect may not have had time to become fully operative before additional reaction chains are initiated, leading to higher rates of oxidation with the larger areas (or amounts) of catalyst. Furthermore, when the precipitation effect has reached its equilibrium point, there will also be a contribution to the sludge value by the extra copper-containing sludge that is precipitated.

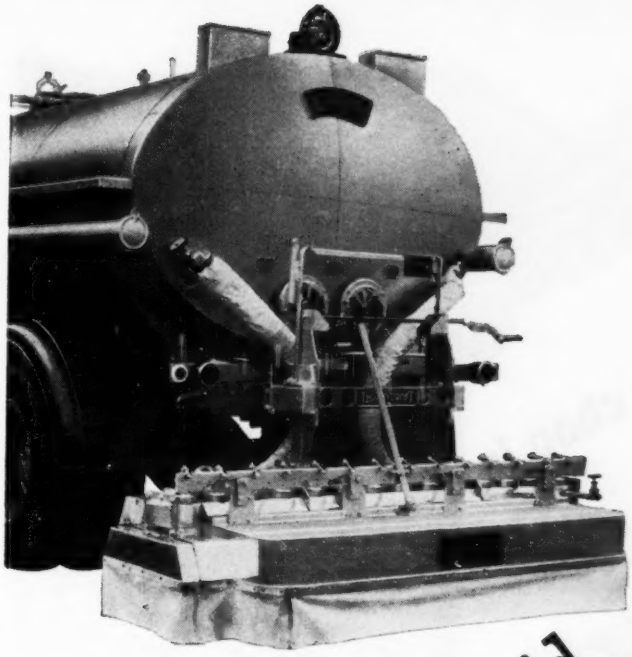
As I explained in presenting my paper, in copper metal-catalysed oxidations the extent of the reactions can be accounted for entirely by the amounts of oil-soluble copper found. What matters is not the amount of copper that dissolves from the metallic catalyst, but the amount that is not precipitated from the dissolved form. This is important, and it brings me to Professor Weiss' second point. On this the paper provides evidence that if one removes metallic copper at an intermediate stage from an oxidizing oil, then one does not affect the rate or extent of oxidation, nor does one affect the concentration of soluble unprecipitated copper.

I would agree with Professor Weiss that the metallic catalyst provides a reserve of copper which can be "dissolved" into the oil—but the vital thing is that word "dissolved" in inverted commas. It may "dissolve" (and even at different rates with different oils), but

it is all precipitated immediately into a catalytically-inactive form of sludge. Each oil seems to know how much catalyst it must precipitate in order to retain the " correct " amount (for that oil) in solution. This seems to happen in precisely the same way regardless of whether one uses a metallic or a soluble catalyst. The oil does not seem to need to know what kind of catalyst the experimenter has used. It keeps the same amount in the soluble catalytically-active form regardless of which catalyst one adds initially.

On Professor Weiss' third point, I think the mechanism that he outlines is a possible one and the kind of thing which probably happens in reality. There may not, of course, be any need to specify an intermediate stage with the soluble catalyst. In fact, since these catalysts are used as oil concentrates, they usually produce instantaneous catalysis, so that the ions are probably present from the start. It may be that Professor Bawn's work on the cupric/cuprous ratio may throw more light on the problem. I have high hopes that it will.

As regards Professor Weiss' fourth point, about making a decisive recommendation as to the most suitable concentrations and areas of soluble and metallic catalysts, I think it is essential that the conditions chosen should be such that they will give self-correlating results lining up with practical performance. This is the key to the whole problem. Bearing in mind the title and objects of my paper, I tried to go as far as was appropriate in establishing what are called " corresponding test conditions." More work needs to be done here before we rush into a quick decision as to the most appropriate catalyst condition for the international oxidation test. The reply that I have given already to Dr Salomon in this symposium discussion summarizes my present views on this subject. I feel sure that we are not far from the end of the road on this matter.



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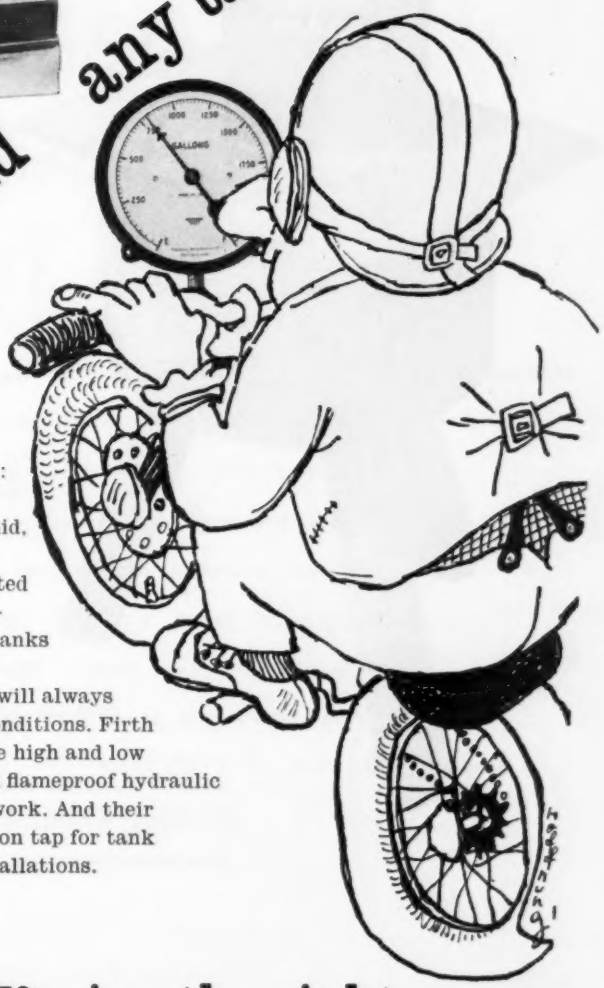

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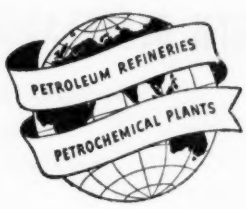
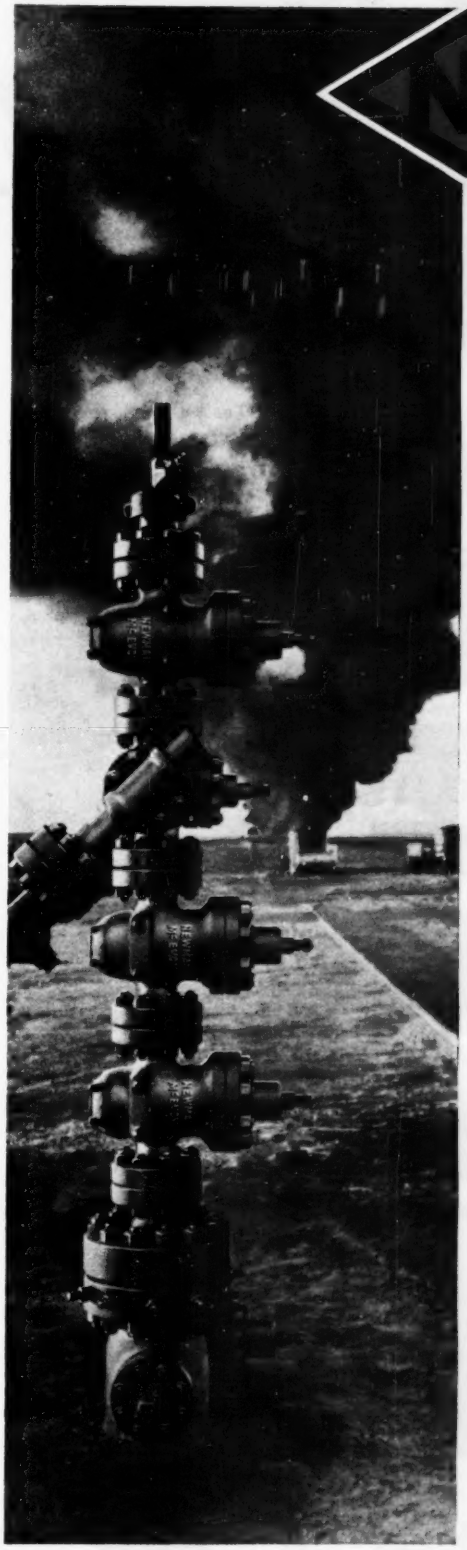
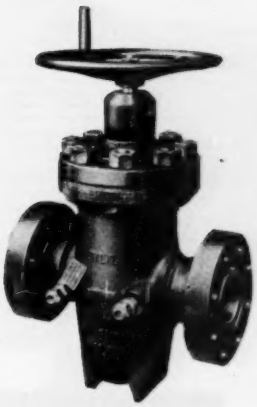




Newman-McEvoy valves at one of the new French wells—Hassi-Messaoud in the Sahara.



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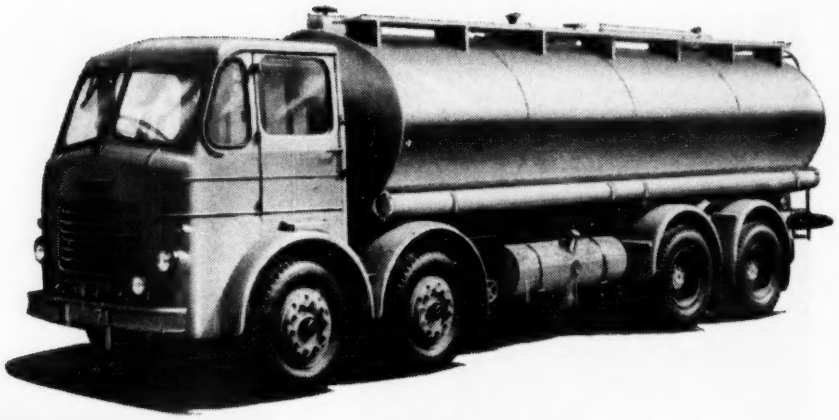

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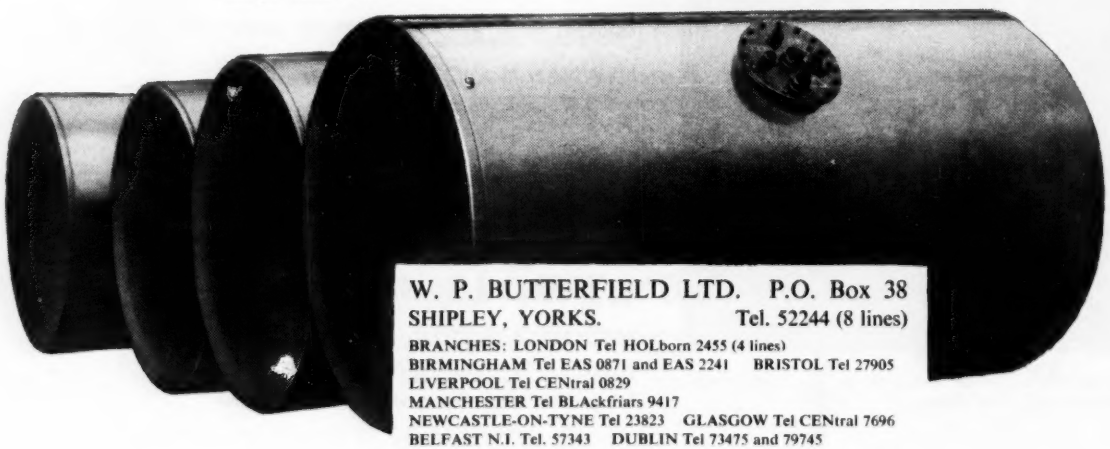

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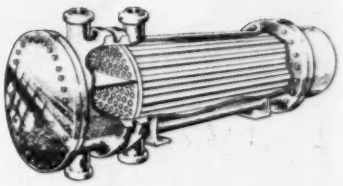

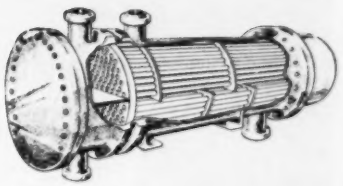

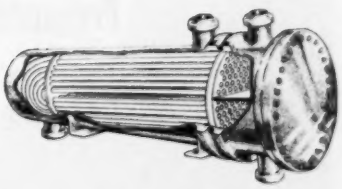

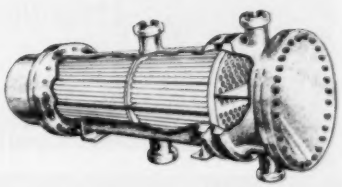

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Philadelphia, Pennsylvania—Work was recently completed on two 26,000 B/SD Platforming® units at Gulf Oil Corporation's Philadelphia refinery by Procon Incorporated. Two 26,000 B/SD Hydrobon® units used with the Platformers were also built by Procon. The Platformer heaters were the largest ever built. Procon engineers recommended single heaters for each Platforming unit instead of two smaller heaters for best use of available space and maximum construction economy.

London, Ontario, Canada—Procon (Canada) Limited recently completed the installation of flaking mills, ovens, conveyors, dust collection systems and related equipment as part of a plant modernization program for Kellogg Company of Canada, Ltd. This construction covered improvements to Kellogg's cereal processing plant at London, Ontario.

Al Kuwait, Kuwait—Work is proceeding on 4,000 B/SD Platforming-Unifining* units and a 7,200 B/SD prefractionator being built by Procon (Great Britain) Limited for Kuwait Oil Company at Kuwait on the Persian Gulf. Work covers mechanical and structural design, engineering, procurement, inspection and supervisory services for Kuwait.

Heide, Germany—Construction was recently completed on a 4,000 B/SD Platforming unit under the supervision of Procon (Great Britain) Limited for Deutsche Erdol-Aktiengesellschaft (DEA). This is part of an extensive reconstruction program, and will supply premium gasoline to Northern Germany and Denmark.

Bakersfield, California—The construction of Mohawk Petroleum Corporation's 925 B/SD Unifining unit was recently completed by Procon Incorporated. This unit processes thermally cracked naphtha derived from California crude. The Unifining unit was built at Mohawk's Bakersfield, California, refinery.

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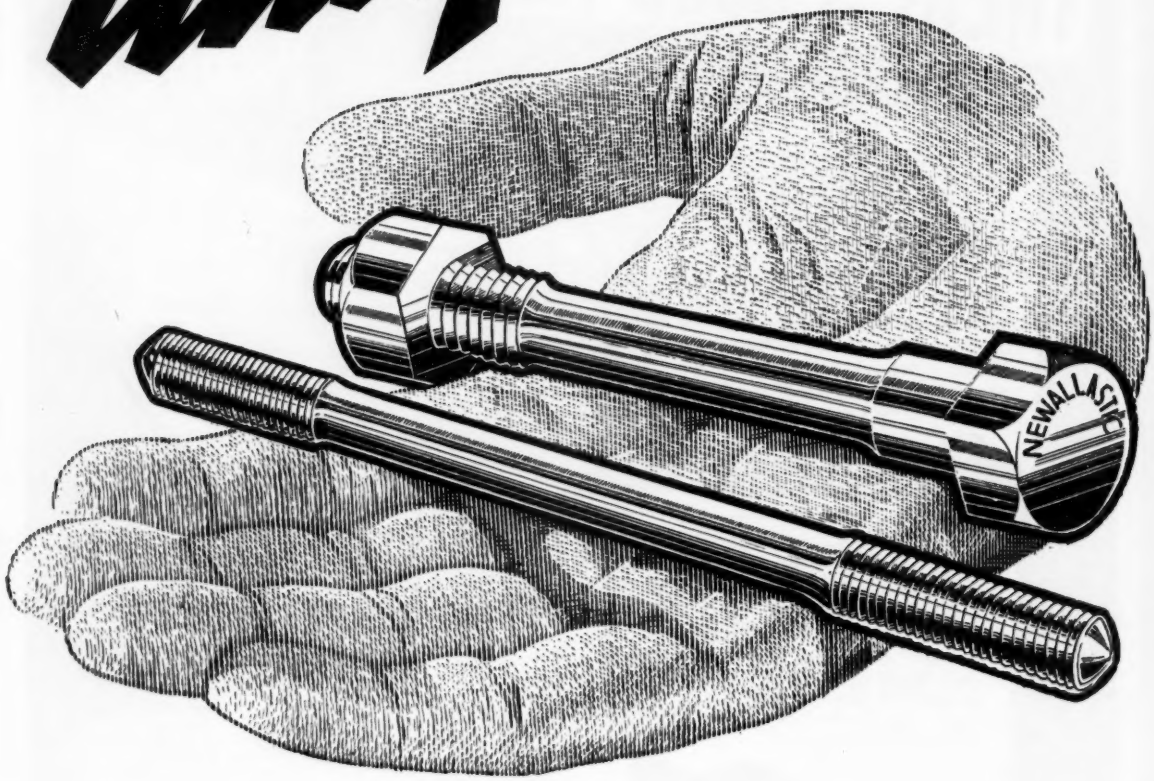

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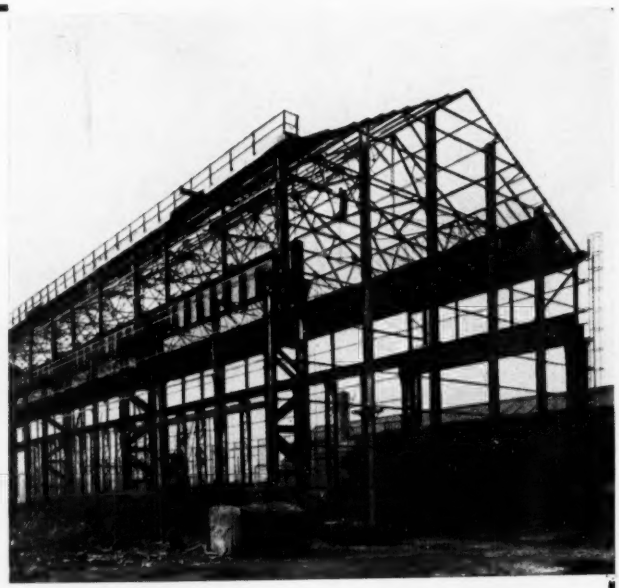

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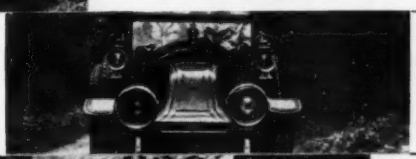
this Filter talk will drive me round the bend!

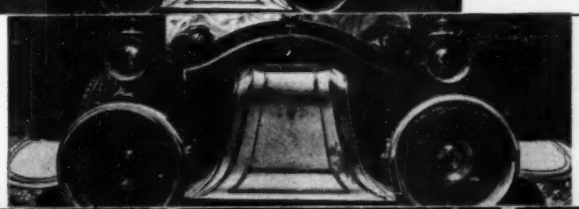
Sorry, old fruit. I was only trying to be helpful.

Helpful! Here am I practising for the only real sporting event of the year and all you can talk about is some wretched little gadget on one of your blasted hairyplanes. Can't you see I need to concentrate?

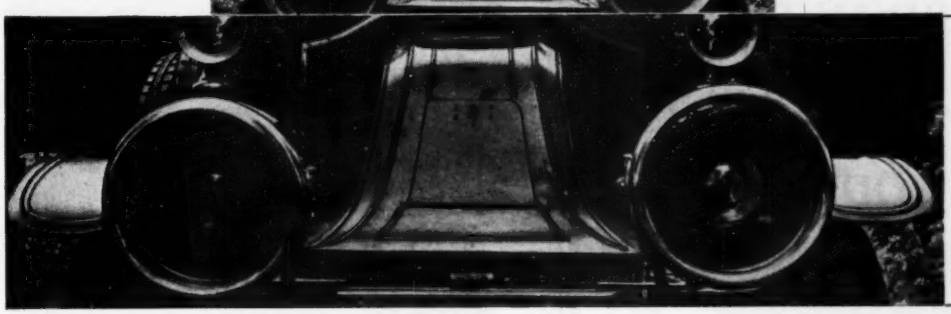


It's not a little gadget and they'd never put it on a plane—it's bigger than this Renault. They put it in the line between the storage and aircraft tanks to make sure the plane gets clean, water-free fuel.

That's the trouble with your infantile modern engines—they have to be fed on strained foods or they get indigestion. Now look at Dotty . . .



Exactly. Do you really think she enjoys having that steam pouring through her exhaust? Now if you took a Simmonds Fram Separator Filter in tow you could have 100% water separation and complete filtration of solids down to 5 microns.



It's tempting, very tempting . . . but it wouldn't be fair on the other competitors. Now d'you mind if we stop a minute . . . I think I really will have to get the rest of that bird's nest out of the tank.

the point of the argument... **FRAM SEPARATOR FILTERS** for clean water-free fuel

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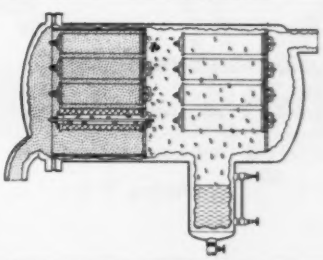

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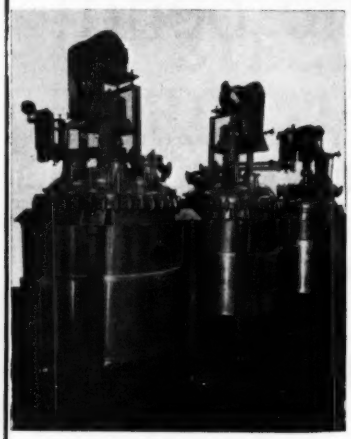

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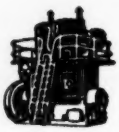

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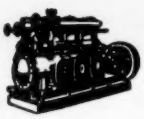

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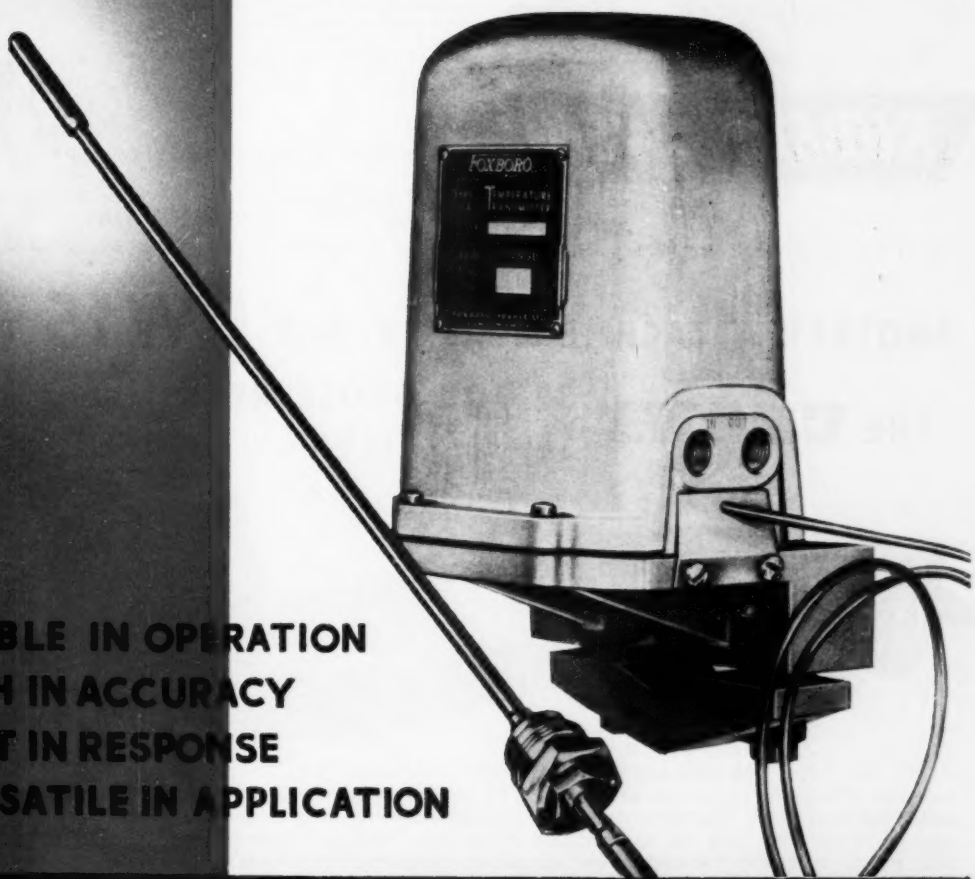

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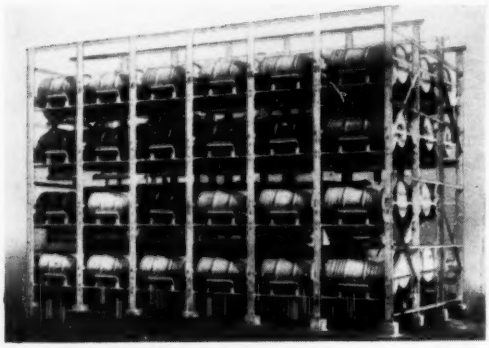

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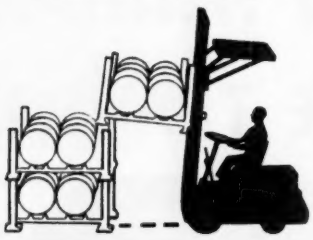

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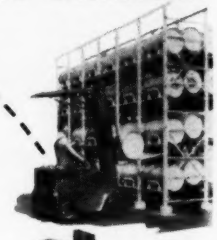
Can be stacked up to 4 high without damage, the load being taken on the posts. Any drum can be readily removed from the stack. Pallet posts are removable to allow drums to be taken off the top of the stack for transportation to the rack.



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The 32-Ton Goose Neck Semi-Trailer (illustrated) is designed primarily for use with the wheeled D.W.15 Caterpillar tractor, the welded arched neck giving the necessary clearance to the tractor's large pneumatic tyres when turning. By using the Crane Goose Neck Semi-trailer, tracked vehicles, heavy machinery, earth moving plant, etc. can be transported without the need of a special towing vehicle, thus saving spares and reducing operational costs.

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